SCIENCE FOR EVERYONE

Ya. A. SMORODINSKY

# TEM-PERA-TURE

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Я. А. Смородинский

# Температура

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# Temperature

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# Preface

A book popularizing physics pursues two goals. First, a reader should be told something he didn't know before. Thus, the present book on temperature speaks of numerous facts which are not mentioned in school textbooks. The book does indeed popularize but not everything it describes will be profoundly understood because attempts to explain some subjects clearly without resorting to mathematics and those areas of physics which are omitted from school texts are not always successful.

There can be only one remedy against this shortcoming, be optimistic! Later you will get to know both statistical physics and quantum mechanics and then everything I describe here will become clear and comprehensible. No bypasses exist on the roads to wisdom: you will get to the summit only by struggling through uphill stretches and mountain passes regardless of the difficulties looming ahead.

Nevertheless, even with some details unknown, it is useful to obtain at the start of a journey some notion about the route and where it leads. A popular-science book is to help in precisely this respect; this is its second, and probably more important, goal.

This book on temperature was written to explain how physical concepts arise, how new methods of measuring physical quantities are developed, and how the progress in physics makes well-worn concepts move into modern fields of physics of which our predecessors were understandably quite ignorant.

The physics of today has grown into a unified science. When trying to study one of its subjects, we invariably cross into adjacent, sometimes very unexpected fields.

The story of how people uncovered the laws of nature and how the majestic edifice of the natural sciences was erected is interesting and instructive. One of the chapters of this story is that about temperature.

I am grateful to Prof. I. K. Kikoin and Prof. M. I. Kaganov for their valuable comments on the manuscript of the book.

Moscow, 1982 *Ya. Smorodinsky*

# Contents

# Introduction

Everybody knows what is meant by heat. School textbooks teach us that the particles in gases, liquids, and solids are in perpetual motion, and that this motion is perceived by the senses as heat. The energy of motion of these particles, averaged over a tremendous number of them, determines the temperature.

Usually everything concerning heat is treated in textbooks in such a clear and simple way that this part of physics may even appear dull.

However, the theory of heat took very long to mature. The questions, What is heat? and What is the difference between temperature and heat? remained unanswered for many centuries. Physics is a relatively young science. The laws of nature appeared to be fairly unrelated rules deduced from observations as recently as two centuries ago. Only mechanics could compete with mathematics in rigor and elegance. Only in mechanics could people derive formulas for an accurate design of mechanisms. The next to mechanics in rigor was optics (what we now call geometrical, or ray, optics). The remainder of the knowledge about nature comprised two sciences: physics and chemistry.

Physicists strove to comprehend the unifying elements of distinct parts of natural sciences. Some of them believed that all phenomena could be explained in terms of mechanics and that everything in nature consists of minute particles: atoms, or monads, or corpuscles (these are equivalent terms predominant in different periods). Others insisted that the primary elements of nature are liquids and that the universe is filled with an all-pervading substance, ether. Heat was also considered a liquid, and the caloric, or thermogen, theory was a very popular foundation of the understanding of heat.

Many physicists saw a connection between heat and the motion of molecules, Mikhail V Lomonosov was one of them. But it was not easy to turn general arguments into a rigorous science.

A natural scientist of that period, studying physics or chemistry, had almost no instruments at his disposal to conduct a quantitative study of nature. He could neither design experiments nor convert the results of his experiments into equations. This was not considered to be the true objective. Before Isaac Newton showed in his great treatise *Mathematical Principles of Natural Philosophy* how his new mathematical method enabled natural phenomena to be translated into the language of formulas, equations, and numbers, scientists had only striven to describe and classify what they observed. From antiquity it had been conjectured that everything in nature was built of atoms and that the motion of atoms caused the properties of substances. When discussing heat scientists argued about what type of motion is manifested in the thermal properties of bodies, and about how it is related to light. They tried to derive the diversity of phenomena from the hypothetical diversity of atomic shapes. From our current point of view the books written by scientists of that period more resemble fiction than rigorous scientific writing. However, one should never judge history by today's criteria. When reading about the history of science we should bear in mind that it does not reduce to the accumulation of facts and creation of new theories. Methods of describing nature change with time, as do the ways of thinking about its laws and even the objectives of science change. Things that may seem naive in the light of our current knowledge were in fact important in the evolution of science. Without this appreciation of history, it might appear miraculous that science could grow at all.

Something extraordinary took place. Although mechanics was maturing in a logical fashion (the motion of planets being found to obey Kepler's simple laws and Newton using them to found celestial mechanics), the science of heat, or thermal phenomena, was developing in a very strange manner. Somehow, all the speculations dealing with atoms seemed, for a very long, unnecessary for the theory of heat.

A theory evolves in a sequence quite different from that in which it is presented now in textbooks. When this story is recounted now, we are baffled for how the theory of heat could be developed without questioning what heat was.

This small book is devoted to the science of thermal phenomena. In order to limit the scope somehow, I chose temperature as the topic. The book tells the story of how the notion of temperature arose and how its meaning evolved when scientists began to understand what happens when a body is heated or cooled in ever more detail.

## Degrees and Temperature

It is interesting to trace the unusual history of how people learnt to measure temperature. Thermometers were invented long before it was understood what was being measured.

When measuring angles between celestial objects, or distances on the Earth, or even time, man knew what he was doing. With temperature it was different. Temperature stems from the very tenuous sensation of warm and cold which people believe is similar to those of smell and taste. But neither smell nor taste are quantifiable (at any rate, exactly quantifiable). Nobody bothers to ask or define how much one dish is more tasty than another, or by how much the smell of hay is different from that of roses. On the other hand, warm and cold objects can always be placed side-by-side and it can be established by touching them which is the warmer.

Man has known from time immemorial that when two bodies are in close contact, they reach what we call now a "thermal equilibrium"

A hand immersed in water warms up (or cools down) to reach the state of the water.

A stove heats the air in a room. A metal rod heated at one end becomes heated as a whole. Flows of heat are found everywhere in nature and the students of nature have always perceived in this the work of puissant natural laws.

Very different opinions have been held about heat flows, thermal equilibrium, and the degree of heating of a body.

The scholars of antiquity and the scholastics of the Middle Ages postulated that there is a correspondence between heat and cold, on the one hand, and attraction and repulsion, on the other, though this definition can explain hardly anything.

Nevertheless, this explanation was not quite that meaningless. On the contrary, the reader must try and get a feeling for the first attempts to find a connection between our senses and specific characteristics of the outside world. It is useful to read what Pierre Gassendi, one of the best minds of the 17th century, wrote about this subject in his fundamental treatise *Sintagma Philosophicum*: "Cold produces a specific and very familiar effect on our senses; and since cold is antagonistic to heat, the atoms corresponding to it must be of a nature opposite to that of the atoms generating the feeling of warmth. Heat characteristically dissociates while cold characteristically contracts; hence, the atoms corresponding to them must have special masses and shapes, move in a special manner, and thus generate what is usually called heat."

Gassendi did not appreciate that particles can move in different ways since at that time nobody knew anything about either the velocity of atoms or their energy. Nevertheless, Gassendi had no doubt that heat could be explained in terms of the motion of particles that nobody even hoped to be able to see some day. This was indeed a daring hypothesis. In this respect Gassendi hardly differs at all from our contemporaries. Indeed, when nowadays we deal with the quarks from which heavy particles are built, we are following the same path for we explain the properties of real elementary particles by the motion of unobservable subparticles.

It is interesting that in the Orient science went through a completely different evolution. Oriental scholars have left us no instruments to measure how hot a body is. They were not looking for an exact description of physical phenomena for the language of formulas and numbers was alien to them, and even unnecessary in their philosophical systems. Their systems had no room for the notion of temperature and both doctors and philosophers were equally happy without measuring temperature.

The first thermometers were brought to China around 1670 by a Jesuit missionary called Ferdinand Verbiest. But there are things that our science has inherited from the Orient. The exotic terms “flavor” and “color” which in modern elementary particle physics denote certain hidden properties of quarks, in Chinese writings stood for the forms of activity of substances, along with sound. A comparison of the two distinct ways of learning about nature, one of which formed in the Orient and the other in the Occident, is instructive. It tells us of how different the different scientific outlooks can be, and how far apart different approaches can diverge. This topic is not simple but fascinating. Alas, it would be too much of a digression and we are forced to return to our proper theme to find out when, and in what circumstances, temperature made its appearance in Europe.

In all likelihood, the ancient physicians were the first to feel the need of a comparative, and fairly precise, scale of body heat. They knew for a long time that a person's health is somehow related to the thermal state of his body, and that medicines are capable of affecting this stage. Medicines were attributed cooling or warming properties and the extent of their action was described in terms of degrees (i.e. steps, in Latin). However, cold and warmth were not regarded as opposite: heat was moderated by moisture, and cold by dryness. A great Greek physician Claudius Galen (2nd century A.D.) taught that medicines must be classified by degrees. There were supposed to be four degrees of heat and just as many degrees of cold. There was also a neutral temperature, that of a mixture of ice and boiling water, and a man's temperament was determined by comparing it with this "reference".

Physicians were not aware that all healthy people have the same temperature. Instead each person was assigned his own personal temperature which depended on his temperament.

Medicines were also classified by degrees. Medicines were able to warm up or cool down a patient, so they were regarded as cold or hot, and were additionally divided into four degrees according to their potency. Medicines were prepared as mixtures that were composed so as to achieve a mixture of a prescribed degree. Actually, Galen gave no quantitative relation between the concentrations of ingredients of mixtures and their degrees nor did he say anything about how to determine the degrees of heat or cold in a mixture. The evaluation was a matter for the skill of the doctor and the problem of how to calculate the degree of a mixture from the degrees of its ingredients was never solved. Nevertheless, medical mixtures left their trace in physics.

In Latin the word "mixture", or rather "mixing", is *temperatura*. However, the word presumably had taken on its current meaning only by the 17th century, along with the appearance of our word "thermometer".

In 1578 Joannes Haslerus published a book *De Logistica Medica* devoted to the problem of determining the degree of a mixture. The author introduced a nine-degree scale. The fourth degree of warmth was considered normal for the body temperature of equatorial inhabitants, and the fourth degree of cold for inhabitants at the poles. Zero temperature was assigned to those living at 40-60° latitudes. Each degree was subdivided into three parts, so that effectively there were twelve degrees for heat and just as many for cold. And the zero was there too. Physicians thus passed on to physicists a twelve-degree scale for thermometers.

Uncertain "degrees" characterizing a heated body were discussed even before Galen. Here Hero of Alexandria, who used the property of air to expand on heating, is usually cited. But the true history of the science of thermal phenomena began with Galileo Galilei.

# Galileo

None of Galileo's contemporaries compared with him in his ability to perceive great laws in simple phenomena. The reader is of course familiar with how much he found out, purely by thinking about the way the bodies fall onto Earth. But it is not as well known that he was one of the first men (and may be the first) to write about the mechanical nature of heat. It is interesting to recall what prompted Galileo to take up this subject.

Two comets were seen over Rome in 1618 and celestial phenomena always stirred up fear or hope. Interest in scientific interpretations of the events was tremendous and people demanded explanations and predictions.

In December of the same year Lince Cesarini wrote to Galileo from Rome: "Even people normally indifferent to everything are excited, and even the laziest of the lazy have jumped from their beds, so you can imagine the tumult caused by the appearance of the two comets and the stupid conversations they have stimulated." A lengthy discussion began concerning the nature of comets. The Jesuits were represented by Horatio Grassi and he was opposed by Galileo's student Mario Guiducci, chairman of the Academy of Florence. Both devoted a great deal of energy to analyzing the general goals of science. Galileo joined in the discussion, publishing a book *El Saggiatore* (*A Balance for Weighing Gold*) in which he gave a detailed exposition of his views on the nature of physical phenomena. The book is regarded as a masterpiece of Italian prose and an incomparable gem of polemic literature.

Among other things, the book mentions the heating of solids by friction and gives other evidence for the mechanical nature of heat. However, Galileo did not know that liquids and even gases can also be heated mechanically. Galileo's analysis was also hampered by a lack of quantitative information about heat.

In Galileo's time there was almost nothing a scientist could measure. Even a simplest measurement of length or volume was difficult because there were no generally accepted units of length. Units of length differed from town to town and any comparison was extremely cumbersome. Time measurements were even more complicated. Of course, sundials, water clocks, and sandglasses existed, but they were absolutely unsuitable for even moderately accurate measurements of short time intervals. Galileo is said to have observed the pendulum motion of a chandelier in Pisa cathedral and measured the period of its oscillations by counting the beats of his pulse. Galileo discovered the laws of mechanics only because he was one of the first to realize the importance of accurate measurements.

When studying thermal phenomena, Galileo used the same approach: he started with a method of measuring a body's temperature.

The thermometers designed by Galileo (around 1597) consisted of a glass sphere $D$ filled with air; the lower part of the sphere was connected to a glass tube partially filled with water and immersed in a jar $A$ also filled with water (Fig. 1).

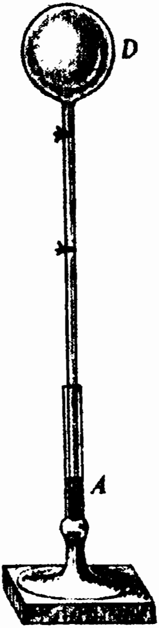

Fig. 1. Galileo's thermometer.

When air in the sphere expanded or contracted, the level of water in the vertical tube rose or fell thus giving a measure of the temperature, say, of a hand touching the sphere. However, the height of the water column in the tube depended both on temperature and on atmospheric pressure, and accurate measurements of temperature were impossible. Galileo's contemporaries knew nothing about the barometer. It was Evangelista Torricelli, Galileo's student, who succeeded in establishing the relation between the height of a mercury column and atmospheric pressure. The very idea that air could exert a pressure on the Earth would have appeared too wild in Galileo's time. Hence, Galileo's thermometer measured something very uncertain; but even this device made it possible to compare the temperatures of different bodies at the same time and in the same place.

A physician and anatomist Santorio Santoro (Sanctorius) of Padua University, although unaware of Galileo's work, designed a similar thermometer and, using this crude device, began recording the temperature of the human body. In his book *Commentaria in Artem Medicinalem Galenis*, published in Venice in 1612, he described how "to measure the hot or cold temperature of the air in all the districts, places, and parts of the body".

Santorio recommended measuring a patient's temperature in a manner quite different from the way we are used to. He did not measure the temperature as such but the rate of increase of the thermometer's readings, that is, the change in the readings during ten swings of a pendulum. In his opinion this procedure revealed the state of a patient's health and quite possibly this is reasonable.

Galileo and Santorio were the first scientists who can be said to have measured temperature in our sense of the word.

The art of manufacturing thermometers was then refined in Tuscany where the Florence Academy pioneered a systematic study of the pressure, humidity, and temperature of air. Thermometers were sealed, were filled with alcohol instead of water, and were operational even when water froze. Florence's craftsmen were extremely skilful, they produced glass thermometers with scale divisions marked by enamel, making it possible to measure temperature to within approximately one degree (in our scale).

The thermometers manufactured in Florence (Fig. 2) were very beautiful, resembling objects of art though, as happens usually, the art declined later. The Academicians of Florence called their academy Accademia del Cimento (the

Academy of Experiment). It was founded in Florence in 1657, but in 1638 Gaspar Enns published a book *Mathematical Wizard* containing a chapter "On the Thermometer, or Drebbel's Instrument, that Serves to Study the Degree of Heat or Cold in the Air" Enn's book is important in that it describes an eight-degree temperature scale and gives the instrument the name "thermometer" This word is also found in a still earlier book, *Les Récréations Mathématiques* by J. Leréchon, published in 1624. Leréchon also described an eight-degree scale in which each degree is subdivided into eight parts. As for "Drebbel's instrument", Enns meant the thermometers made by Galileo's compatriot Cornelis Drebbel who studied the thermal expansion of gases (Fig. 3).

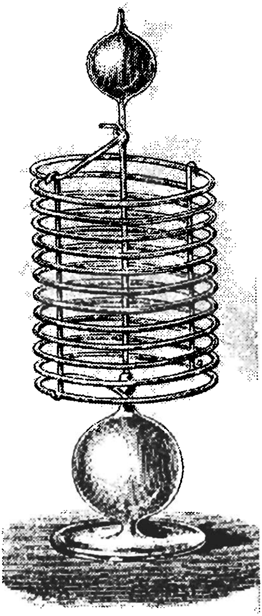
Fig. 2. A thermometer manufactured by Florence's craftsmen.

It cannot be excluded that Drebbel invented his thermometer independently. He had thoroughly studied the expansion of bodies and even designed an engine driven by an expanding liquid (it was called the *perpetuum mobile*

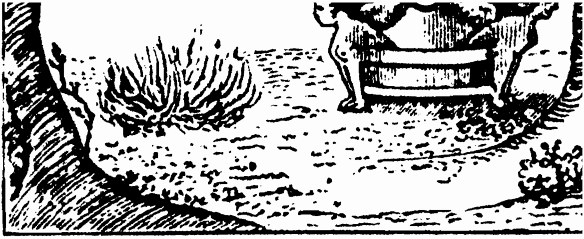

Fig. 3. "Drebbel's instrument".

because no human participation was quired).

A physician, philosopher, and mystic, Rob Fludd, was another illustrious personality w contributed to the invention of the thermomet At the beginning of the 17th century he describ a number of instruments, including a twel degree thermometer.

The history of the thermometer owes much one of the most impressive personalities of 17th century, Otto von Guericke. Despite position as Burgomaster (Mayor) of Magdebu and his frequent diplomatic travels all o Europe, Guericke made a valuable contributi to science. His experiment with the Magdebu hemispheres that sixteen horses could not tear apart is in the annals of physics. In order to remove that air from the sphere, Guericke invented the first vacuum pump. He also designed the first barometer, similar to Galileo's device but with a very long tube. In contrast to Galileo's instrument, Guericke's barometer had the air evacuated from the inner space, and the water filled both the tube and a part of the glass sphere. The barometer was installed on the outer wall of a house, and air pressure was marked out on a scale pointed at by a finger of a wooden angel floating in the glass sphere. Guericke was the first to systematically measure atmospheric pressure and tried to find a correlation between the pressure changes and the weather. It is funny that Guericke called his apparatus the "perpetual motion machine" (*mobile perpetuum*).

It is not surprising that Guericke also constructed a fairly good thermometer. It consisted of a brass sphere filled with air, and a U-shaped tube filled with alcohol. As in the barometer, the temperature was indicated by a wooden angel linked by a string and pulley to a sealed brass box floating in the open end of the thermometer (Fig. 4).

Guericke's thermometer was also fixed to the wall of his house. He wanted to know the air temperature in some absolute units in order to be able to compare temperatures in different places. To achieve this, Guericke had a point in the middle of the scale of his thermometer where the pointer indicated when first frosts set in, the point chosen by Guericke being the reference point (origin) of his scale. The choice was ob-

Fig. 4. Guericke's thermometer and barometer.

viously naive, but a first step had been made.

The boiling temperature of water was firs mentioned as a possible reference point of thermometer scale by Christian Huygens in 1655 He wrote that with this choice it would be possible to compare temperature (he called it th "observable degree of heat") at different place without moving the same thermometer fron place to place.

We should also mention Newton's paper "O the Scale of Degrees of Heat and Cold", pub lished in 1701, which describes a twelve-degree temperature scale. Newton placed zero where we place it nowadays, i.e. at the water freezing point, and 12° corresponded to the temperature of a healthy human. Newton thus very clearly formulated the idea of a temperature scale although other physicists of his time also seem to have been on the verge of doing the same. Still, the thermometer had not yet reached the stage of being instrument for physics.

A long time was required for the idea of constant points on the temperature scale to take root. In 1703 Guillaume Amontons, commenting Newton's work, described a new thermometer in the memoirs of the Paris Academy. This thermometer did not measure the increase in the volume of the air upon heating, but measured the change in its pressure and so the air was locked in by a mercury column. In his new thermometer Amontons introduced constant reference points: the boiling point of water (he did not know that this temperature depends on pressure) and, however, surprising it may sound, he chose for his zero "that considerable degree of cold" at which air becomes devoid of all its elasticity. The point he chose for this "absolute zero" contained a large error, namely, about 240 °C below zero on the modern scale. Nevertheless, it was quite an achievement. Finally Amontons was able to construct a completely sealed thermometer thus making its readings independent of atmospheric pressure.

The first modern thermometer was described in 1714 by Gabriel Daniel Fahrenheit, a glass-blower from Holland. His contemporaries were surprised to find that Fahrenheit's alcohol thermometers all agreed with themselves. Fahrenheit's secret was that the divisions on the scale were made very accurately, by using several reference points. Fahrenheit imitated the lowest temperature of the harsh winter of 1709 by a mixture of ice, common salt, and sal ammoniac. The second reference point was obtained by immersing the thermometer in a mixture of ice and water. The distance between the two points was divided into 32. Fahrenheit tested his scale by measuring the human body temperature and this new point was 98 °F. Later Fahrenheit introduced the fourth reference point: the boiling point of water which he found at 212 °F.

Different Fahrenheit thermometers could be calibrated by comparing them at different reference temperatures and they became famous for their accuracy. The Fahrenheit scale is still used in Britain and the USA.

The scale that gained general recognition in France (around 1730) was that of Réaumur and was based on the freezing and boiling points of water (0° and 80°). René Antoine Ferchault de Réaumur determined experimentally that water expands by 0.08 (the correct figure is 0.084) between these two points. Soon alcohol was replaced with mercury whose thermal expansion coefficient is less dependent on temperature than that of alcohol.

The centigrade scale we use now was suggested in 1742 by the Swedish astronomer Anders Celsius. He disliked negative temperatures and thought it would be expedient to reverse the conventional scale, placing the zero at the boiling point of water, and 100 °C at its freezing point. But the "reversed scale" was never popular and was very soon returned to the original form.

A few words can be added about a thermometer with Delisle's scale. The mercury thermometers of the Petersburg Academician Joseph Nicolas Delisle were very popular in Russia in the first half of the 18th century. Their scale was divided into 150. The thermometers were well made but soon lost out to Réaumur thermometers.

In Russia the standard temperature scale up to 1917 was Réaumur's and Réaumur thermometers were installed in streets and in most houses. It was only in the thirties they were replaced with Celsius thermometers.

In Britain and the USA people still use Fahrenheit thermometers, and anyone used to the centigrade scale should not be startled when he reads that meat should be roasted at 350-400 °F or that the 98 °F body temperature of a child does not worry his mother.

Whatever the choice of thermometer scale, one degree remained a more or less arbitrary quantity. It was defined by dividing the scale into equal parts, so that it was not possible to determine the behaviour of the expansion coefficient at different temperatures since the degrees at freezing point and at boiling point are thereby identical. Not a single paper was published that considered the relationship between temperature and the properties of substances, except thermal expansion, and incidentally even this was rather poorly investigated.

## What Is Heat?

The thermometer became a standard instrument at the beginning of the 19th century, but the generally accepted point of view as to what it was that a thermometer measured was only formulated much later.

By this time the properties of gases had been known rather well. The relation between the pressure and volume of the gas was clear as early as 1662. The famous law that we call Boyle's law (also known as Mariotte's law) was in fact found by Boyle's pupil R. Townley who thought of comparing two columns on numbers in the laboratory log of his teacher. Mariotte only published his paper in 1679. The law relating gas volume to gas temperature was discovered in 1802 by John Dalton and Joseph Louis Gay-Lussac. It was not easy to formulate this law accurately because it called for an ability to measure temperature rather well. Hence, the coefficient $\alpha$ in Gay-Lussac's law $V = (1 + \alpha t) V_0$ ($V_0$ is the volume at $t = 0$ °C) was for a long time known with a considerable error. Gay-Lussac estimated it to be $\frac{1}{266}$, Carnot estimated it to be $\frac{1}{267}$, and Mendeleev used the almost modern value of $\frac{1}{273}$.

But having learnt how to measure temperature, physicists did not go too far in understanding what heat was.

Even in mechanics there was a confusion between the distinct concepts of force, energy, and momentum. In the 18th century there were heated discussions about whether the kinetic energy or momentum gives a measure of motion. Kinetic energy was for a long time called the "live force", in contrast to the "inanimate force", such as the energy of a wound-up spring.

It was even more difficult to separate the concepts of "heat" and "temperature" When a body is heated, its temperature increases. When heat flows from one body to another, the temperature of one body diminishes and that of the other increases.

In many cases heat behaves like a stream running down from a hill to a valley. The similarity between heat and a fluid became even more conclusive after electricity had been discovered because electric current also flows through wires like a river, levelling off the potential difference between two charged bodies.

In 1893 the French physicist L. M. Brillouin wrote: "As far as I am concerned, I am still convinced that the definition of the temperature of a body as the amount of energy, potential or kinetic, total or partial, of only the standard matter, is in error. Temperature thus defined, although rather simply related to the thermodynamic properties of gases, does not seem to be related in any way to the conditions of equilibrium in the case of radiation into the space free of matter. In this last case the inevitable role of ether has led Monsieur Boussinesq to a completely different definition of temperature. This definition is very little known but, from my point of view, is much more satisfactory and fruitful... ."

Let us have a look at the definition of temperature so appealing to Brillouin.

In his long-forgotten paper "The Study of the Principles of Mechanics, Molecular Structure of Solids, and the New Theory of Ideal Gases" which was published in 1773, Boussinesq gave the following definition of temperature: "The absolute temperature of a small volume of ether can be defined as one half of the live force that it possesses per one unit mass, or an amount proportional to it." Now it is not easy to read any meaning into this definition, and I give it only in order to emphasize how difficult it was to understand concepts that later grew to be so simple.

Still, it is possible to understand how such obscure statements could be written. Indeed, in addition to gases which are rather easily modelled as collections of molecules (this was the opinion of the majority as early as at the end of the 19th century), there was also radiation. The radiation emitted, for example, by the atoms of a gas carries energy, and the intensity of radiation (or the distribution of energy over wavelengths of the spectrum) is determined by the temperature of the emitting gas. The energy of radiation seemed unrelated to the atoms and it was very difficult to comprehend its nature.

The problem of determining the distribution of energy over the spectrum was also extremely hard to solve. It was a challenge to the best physicists of that period. We shall return to this problem, but right now the reader is merely invited to get a feeling for how tremendous the obstacles were in the way of an explanation of the fate of the energy transmitted by the gas to the radiation. At that time electromagnetic waves were regarded as oscillations of the world's ether, which was assumed to fill all space continuously. Hence, this ether was thought to be the carrier of thermal energy and, as a result, the carrier of temperature as well.

The progress of science is an extremely interesting and complicated process. The charm of the chosen path can be admired only when the destination is reached; at the start science looks like a maze in which all passages end in cul-de-sacs. Unfortunately, lessons drawn from the history of science often do not bear fruit: new researchers start along wrong paths just as sure of themselves and the ones who succeed in finding a true approach are only those who overcome the conservatism of traditional thinking.

The difficulties with radiation did not arise out of blank space. At the end of the 19th century William Thomson (Lord Kelvin) could not understand what portion of the energy of a gas was taken by the vibrations of molecules. A molecule was thought to be a small elastic sphere consisting of a complex coil of springs each of which takes its own part of energy. But this model was in clear contradiction with experiment. The amount of heat required to heat a gas, i.e. the heat capacity of the gas, was such as would be required by molecules moving as solid wholes; practically nothing was left for vibrations. Kelvin was completely baffled and was even inclined to think that the theorems about the kinetic theory of heat, discovered by James Clerk Maxwell, were wrong. Kelvin was very worried by this unpleasant situation. He regarded it as one of the two clouds that darkened the clear skies of physics on the eve of the new century. The failure of Michelson's attempt to detect the motion of the Earth relative to the ether through which light propagates was, Kelvin considered, the second cloud. He was right, these two paradoxes indeed concentrated on the critical stresses points. They were resolved only with the advent of the revolution in physics and with the establishment of quantum and relativistic principles.

We shall return to the kinetic theory later but we underline here that is was not easy to get used to the notion of moving atoms that is so much of a habit for us nowadays. Difficulties crept up from different directions. Various types of motion are possible. Particles can move translationally; they can vibrate around an equilibrium position; and finally, they can rotate. It proved difficult to find out which of the motions is related with heat and which with light. Galileo believed that different phenomena correspond to different sorts of particles whilst other physicists deduced heat from translational motion (this was the opinion of Bernoulli, for example). It is thus clear why Kelvin was looking in this direction when he was trying to solve the puzzle. A still more formidable obstacle was the lack of an explanation of the nature of electromagnetic radiation which carried energy but behaved quite differently from an ensemble of atoms and seemed to form a continuum.

The paradoxes involved in the radiation spectrum and heat capacity of the molecules looked like a trap cleverly set by nature. Physicists faithful to classical physics could not find a way out of this trap. Kelvin attempted to show that thermal motion does not excite molecular vibrations and believed that he had given a "final proof" of the failure of Maxwell's kinetic ideas. Kelvin was of course unaware that classical physics could not in principle resolve the paradoxes that have been discovered. The solution only came with Planck's quantum hypothesis.

Walther Hermann Nernst had started along the correct way even before Planck's discovery. He was the first to realize that some types of motion do not have "equal rights" in the partitioning of energy, being "frozen out" at low temperatures and entering the picture only at high temperatures. These ideas enabled Nernst to predict the behavior of things in the vicinity of absolute zero, although the actual meaning of his prediction became clearer much later in quantum mechanics. We shall see later how these ideas of Nernst have transformed the concept of the "number of degrees of freedom", which looks so trivial in classical mechanics.

Planck and Nernst were physicists of the older generation who were enthusiastic about the novel ideas of the 20th century. It was to them that Einstein owed the introduction into the community of the best minds in physics. Both lived to see their ideas incorporated into the grand edifice of quantum physics.

## Thermal Equilibrium

The concept of "thermal equilibrium" is very often encountered in the theory of heat, and we need to discuss it briefly before going on with our story. Thermal equilibrium is most easily understood in the case of a monatomic gas. If the gas in a container behaves such that its temperature is the same at all points in the container (obviously, the temperature of the walls of the container is also always the same), then the gas is in thermal equilibrium. This means that the gas's heat does not flow from one part of the container to another, and neither the pressure nor chemical composition changes. From the standpoint of classical thermal phenomena, therefore, "nothing happens" in this gas.

The fact that heat always flows from a hot body to a colder one, that is, that the temperature of bodies brought into contact always tends to level off, must be regarded as a fundamental natural law. In mechanics, processes can follow different paths, e.g. a pendulum may swing in different planes, or a wheel can be rotated in any direction. The situation is quite different in the case of heat for a hot kettle in a room cools down "of itself", but cannot warm up "of itself"; in order to freeze the contents of a refrigerator, work has to be done. A room can be heated by an electric radiator, but the radiator cannot be heated up at the expense of cooling the room.

Heat invariably flows so that temperatures level off and a system reaches a thermal equilibrium. The transition to thermal equilibrium may be a complicated and rather protracted process.

We say that a container is thermally insulated if the heat flow is minimized—that is the principle of thermos flasks. More complicated situations are possible. In a hot plasma the temperature of the electrons may differ from that of the ions (as if we had a mixture of gases at unequal temperatures) and the two temperatures level off rather slowly. Hence, one point in the plasma may be at two temperatures at the same time. Each of the two systems, that of electrons and that of ions, is in thermal equilibrium: electrons with electrons and ions with ions but the heat flux between ions and electrons is very slow. We shall come across such flows when discussing the Universe or the magnetic cooling of crystals.

Now let us emphasize again: in nature two bodies in contact tend to assume the same ultimate temperature. If energy is not fed into a system as heat or in other form, the system reaches a thermal equilibrium in which heat flows finally die out.

## Heat and Cold

Different opinions have persisted through history on what heat is. In 1620 Francis Bacon systematized the information on the sources of heat and cold and listed them in tables. Among the entries one could find lightning and summer (or heat) lightning, flame and will-o'-the-wisp, as well as aromatic herbs which produce the feeling of warmth when digested. From all this Bacon somehow came to a conclusion that heat is "expanding motion" In 1658 Pierre Gassendi published his treatise and contended that heat and cold are distinct forms of matter. He believed the atoms of cold to be sharp-angled (shaped as tetrahedra) and to solidify a liquid when penetrating it.

Physicists were mostly hostile to the notion of atoms. The caloric theory which assigned to heat the properties of a liquid flowing from one body to another seemed much more comprehensible. The caloric was similar to phlogiston, a hypothetical substance of flame, and sometimes they were even confused. Caloric appeared to give a conclusive explanation of thermal phenomena. In chemistry the burning and oxidation of matter could be explained by the release of caloric. The caloric theory became generally accepted in the last quarter of the 18th century. One of natural scientists of that period wrote: "...light was ascribed two properties: its ability to illuminate and its ability to heat. Those who considered light to represent vibrations of ether believed that heat also consisted of similar vibrations and of motions generated by the ether in the particles of a body. But recently heat has become to be regarded as something distinct from light and not as its direct effect."

The caloric theory (nowadays we would say "the caloric model") explained a wealth of facts. The theory of the heat engine developed by Nicolas Léonard Sadi Carnot was based on the caloric model. However, the model failed when tested by the law of conservation.

If heat were a liquid of some sort, it would be conserved in the flow so the amount of it would always be constant. This was indeed the contention, the amount of heat taken from the heater is equal to that gained by the heat sink.

At first glance, the statement is correct: a kettle cools down, the air warms up. But quite often this is not the case.

The first to notice this was Benjamin Thompson (later Count Rumford). He was observing the drilling of artillery gun barrels in Munich Armory. Nobody before him had seriously analyzed the causes resulting in the heating-up of the barrels and Rumford tried but failed to do so. The only solution seemed to be that the chips contained less caloric than the initial ingot, and the excess was released by drilling. But then it would be easier to heat the chips than a solid piece of metal since the chips thus had a lower heat capacity. Alas! This was in flagrant contradiction with experiment.

A still greater difficulty lay in the fact that blunt drills "generated" more heat than sharpened ones. Drilling was somehow capable of generating an almost unlimited amount of heat. The simple model of caloric flowing from one body to another was obviously inadequate in these phenomena. The balance was tipped in favor of relating heat with motion. Unfortunately, at the end of the 18th century the accuracy of experiments was still very poor, and although Rumford was supported by Sir Humphrey Davy and Thomas Young who also stressed the role of the vibration and rotation of molecules in all substances, few were dissuaded by the gun drilling evidence.

But a theory is bound to remain sterile as long as its hypotheses remain mere words and are not converted into numbers and formulas. The relationship between energy and heat was established experimentally by James Prescott Joule in 1873; it was a quantitative relation between work and heat. Joule demonstrated that stirring a liquid with a stirrer and thus heating it, 460 kgf·m of work have to be spent for each kilogram-calorie acquired by the liquid (in another series of experiments Joule obtained the figure 423 kgf·m). Julius Robert von Mayer, using the results of Gay-Lussac's experiments on the expansion of gases into vacuum, had calculated this quantity somewhat earlier than Joule but less accurately (365 kgf·m/kcal).

At this stage the model of a nondisappearing liquid, the caloric model, was a hindrance to further progress and was quickly removed from the stage. The caloric model also met with another difficulty. If caloric is a liquid that does work when flowing from a higher level (higher temperature) to a lower level, it was difficult to understand what happens in a nonuniformly heated body as the temperature equalizes. Namely, what happens to the work produced by this flow of caloric?

At that time heat conduction was interpreted as a sort of wave motion in a body, transferable from one body to another.

But even if the "loss" of work went unnoticed, the concept failed to explain how heat is transferred through a vacuum, for instance, from the Sun to the Earth. Vibrations of ether were mentioned, but no conclusive theory could be constructed in these terms. The caloric theory was losing one battle after another.

Many natural scientists discussed the idea of the link between heat and motion. Rene Descartes made relevant statements and Daniel Bernoulli tried to derive a formula for gas pressure.

The British physicist Robert Hooke must be specially mentioned. We mostly remember him as the author of Hooke's law of elasticity. Hooke was truly a spectacular scientist of the 17th century. Boyle's student, he greatly influenced his teacher with his ideas and apparently Hooke knew about the law of (universal) gravitation independently of Newton (their contemporary Sir Christopher Wren had also mentioned it). He paid much attention to studies of optics. Hooke expressed quite clearly the relationship between heat and motion, that is, the vibration of particles in a heated body. Unfortunately, Hooke was advancing brilliant hypotheses without being able to "translate" them into the language of mathematics. Consequently, the discovery of the law of gravitation became the accomplishment of Newton, and for the same reason Hooke's name is not mentioned among the founders of the theory of thermal phenomena.

I have already mentioned that Mikhail Lomonosov also expressed the right ideas, and many philosophers, including Thomas Hobbes and John Locke, identified heat as motion. Let us mention that Locke was probably the first who wrote (around 1700) about the maximum degree of cold which "...means the cessation of motion of imperceptible particles... ." But these philosophers also could not turn uncertain statements into a physical theory verifiable by experiment.

The greatest progress was achieved by Maxwell. The kinetic theory of heat that he had developed made it possible to understand thermal phenomena in terms of classical mechanics. Maxwell derived a formula for the velocity distribution of moving particles which made it possible to calculate certain constants characterizing the properties of matter, such as heat conduction and viscosity of a gas, and to find their temperature dependencies.

In much the same way as Newton created celestial mechanics, Maxwell was the founder of statistical physics (called the kinetic theory of gases in the 19th century).

But Maxwell too had his predecessors. The first formula of the new theory of heat was derived long before Maxwell. But, as happens with "premature" discoveries, the formula went virtually unnoticed. Later we shall return to the work of Waterston, but now we should resume the story of the thermometer and temperature.

## Temperature Scale

In all instruments devised in the 18th century to measure temperature, the measurements in fact consisted in finding the length of the column of water, alcohol, or mercury. Of course, two identical thermometers could be made and adjusted always to give identical readings, but the thermometers only worked in a limited temperature range. The thermometer-filling liquids froze and boiled, and the thermometers could not measure very low or very high temperatures. Besides, it would have been useful to know the relation between degrees in different ranges of the scale. By measuring the amount of heat required to raise the temperature of a body by one degree, for example, at room temperature and at

1000 °C, one could not deduce the relation between the degrees at these points. Two problems faced the incipient science of thermometry. First, it was necessary to choose "reference" points, that is, conditions corresponding to certain chosen points on the scale of a thermometer, such as the origin of the scale, and, second, to construct a definition of the degree that would be independent of the choice of thermometer and be usable to reconstruct the scale at any place on the Earth and at any time.

The Celsius scale accurately fixed two points, 0 °C and 100 °C, with the distance between them divided into equal parts. But the role played by each division remained obscure. It was necessary to understand what happens in a body when the mercury column in a thermometer (placed in contact with this body) rises one additional degree. The simplest assumption would be that the energy of the body (or the heat contained in it) is always incremented by the same amount. This quantity for a unit mass of the body is called its specific heat.

We know, however, that different bodies have different specific heats, and even in the same material the specific heat is a function of temperature, that is, at different temperatures the amount of heat needed to raise the temperature of a body one degree is different. Hence, ordinary materials are unsuitable for this purpose.

It is, nevertheless, possible to devise a body which, to a certain extent, possesses the required properties. This is the ideal gas whose pressure, by virtue of Gay-Lussac's law, is linearly proportional to temperature (at constant volume).

Real gases behave very nearly like an ideal gas if the pressure, and as a result, the density of the gas is very low.

Obviously, the method cannot be used at some temperatures and pressures because at some point any real gas stops behaving like the ideal gas.

Nevertheless, the gas thermometer (usually the hydrogen thermometer) serves as the reference instrument at almost all temperatures feasible in laboratory conditions.

The question of how to determine temperature in a more rigorous manner still remains.

If temperature is a physical quantity, there must be a method of determining it which, at least in principle, is independent of the material chosen to design the thermometer. This problem became solvable only after the advent of thermodynamics. The solution was found by Rudolf Julius Emmanuel Clausius in 1848 on the basis of Carnot's theory of heat.

## Carnot

The theory of heat has a definite year of birth. In 1824 a book was published in Paris by the young engineer Sadi Carnot: *Réflexions sur la puissance motrice du feu et les machines propres à développer cette puissance* (*Reflections on the Driving Force of Fire and Machines Capable of Developing this Force*). But this really great work was noticed by practically nobody. Not one of the leading scientists responded to its publication, and not one heeded the declaration made in the book: "...in order to analyze the principle of obtaining motion from heat in all its entirety, it must be studied of a specific thermal agent, and arguments must be valid not only for steam engines but also for any imaginable heat engines, whatever the substance used as the agent, and in whatever the way the substance is utilized."

The programme we formulated in these phrases was exceptionally daring. Probably, only the discovery of the law of inertia is comparable to Carnot's discovery.

Carnot died in 1836, still unaware of any response to his work. The natural scientists of the 19th century could be stone-deaf when new ideas were proposed. Thus, nobody responded to Riemann's lecture "On hypotheses which lie at the foundation of geometry", and nobody recognized the genius of Oliver Heaviside when he developed operational calculus.

In 1834 Carnot's paper, or memoir as papers used to be called, was revised and reprinted by Benoit Clapeyron in the journal of the Polytechnical School in Paris. In his presentation, put in more rigorous mathematical framework, Clapeyron introduced the graphical representation of thermal processes. The currently popular curves, such as isotherms and adiabats, can be traced to Clapeyron's work.

Carnot's memoir was rejected by the editor of the leading physics journal *Annalen der Physik*, Johann Poggendorff. The same journal rejected Mayer's paper (to be true, it was written quite badly). But Clapeyron's memoir impressed Poggendorff so much that he translated it himself into

German and published in Poggendorff's *Annalen*. Alas, Carnot's ideas found no followers in this form either. Clapeyron's paper was reprinted in German again nine years later, and again this was not the time for recognition. Only at the beginning of the 1850's, more than a quarter of a century later, were Carnot's ideas understood. Together with the law of the conservation of energy discovered by Robert Mayer (in 1843), they were at the foundations of the studies of William Thomson and Rudolf Julius Emmanuel Clausius which mark the birth of thermodynamics.

It is clear from Carnot's diary, published by his brother after Carnot's death, that Carnot already knew about the conservation of energy. In his notes Carnot calculated the mechanical equivalent of heat, obtaining 3.6 joules per calorie (the correct figure is 4.2).

If Carnot had had time to publish his results, the law of the conservation of energy would have become known almost two decades before the work of Mayer and Joule which we shall discuss in later sections. Moreover, his main achievement would have been more comprehensible if the law of the conservation of energy were included in it. But in his memoir Carnot made no mention of the relationship between heat and work. He shared the opinion that thermal phenomena implied a flow of caloric and built up his argument on a wrong premise. Nevertheless, he managed to come to a correct solution. I think that Carnot's work represents a spectacular example of physical intuition.

Let us try to follow Carnot's line of reasoning in some detail.

Carnot formulated the following questions: How does it happen that a heat engine produces work and what is the limit on this work? Different heat engines work differently, one may be more efficient, producing more work, another is less efficient. But can the efficiency of a heat engine be improved indefinitely?

## Ideal Carnot Cycle

The questions as formulated above could be answered only after quite a few concepts had been refined. To begin with, it was necessary to realize that a heated body cannot alone do any work. In order to construct a heat engine, it is necessary to have, in addition to a heated body (the heater, or hot body), a second body at a lower temperature (the heat sink, or cold body).

The hot body of a standard steam engine is a boiler in which water is vaporized and the heat sink is a condenser in which the steam, having done some work, is condensed and thus converted back into water. In addition to a hot body and a heat sink, the engine must include a working substance or agent, that is, a liquid or gas which transfers heat and produces work "as it goes" Carnot explained the appearance of work by a flow of caloric from the hot body to the heat sink. The flow of caloric can be compared with a flow of water running through a dam and rotating a turbine of the electric power station. The amount of caloric is conserved (as well as the amount of water), and what changes is the "level" of caloric as determined by the temperature.

Caloric thus flows from the hot body to the heat sink and thereby produces work. However, if we extend this caloric-water analogy, we soon end in a blind alley. According to the analogy it would be logical to assume the work done by the "downflow" of caloric to be proportional to the temperature difference (like a hydraulic head). We cannot accept this conclusion. Indeed, if this were so, a steam engine would be nonsensical. Once the steam had expanded, done the useful work, and condensed (or simply cooled down), one has to heat it up anew and make it work once again. Heating would require exactly the same amount of work as was produced at the cooling stage, and even then only if all our devices had worked without losses.

Now imagine that somebody decided to build a hydroelectric power station on the shore of a mountain lake, releasing water through a turbine into another reservoir, for instance, another lake at a lower altitude. In order to prevent a drop in the level of the upper lake, he decides to restore the level by pumping the water uphill. This idea is obviously idiotic; the work done by the pumps cannot be less than the work done by turbines. Actually, part of the work will be lost on friction in the turbine, on evaporation of the water, and on some other processes as well. Whatever the design of the pumps, whether they are connected in series or in parallel, the law of the conservation of energy forbids any useful device to be built which is meant to gain something from this enterprise.

Why then do the compression and expansion of a gas in a heat engine yield useful work?

What is the difference between the operation of a hydroelectric power station and a heat engine?

This discussion leads us back to the question that was posed earlier, namely: Are the degrees at different parts of the thermometer scale equivalent? If water in a mountain river falls a height of one meter, it is immaterial whether the meter is in the valley or high up in the mountains because the work yielded by one liter of water falling one meter is the same. This obvious result can be reformulated. We can say that by measuring the energy released by falling water we are only measuring the difference between its levels, we are not measuring the altitude at which the process takes place.

Losses are inevitable; thus, the kinetic energy acquired by water falling a considerable height onto the turbine blade is almost totally dissipated in the impact on the turbine blades.

In order to reduce these losses, velocity of the stream has to be reduced and this inevitably diminishes the turbine's power. Hereafter we shall see again that reversibility entails infinitely small power.

In the case of heated steam the situation is quite different, and that was the first of Carnot's observations. The work that can be done by steam cooling from 100 °C to 99 °C is not equal to the work done by the same amount of steam cooling from 50 °C to 49 °C. The reason is that the steam pressure is different in these two cases.

But in addition to the hot body and the heat sink there is also the working medium, or substance. Could something depend on its properties as well? Carnot found that the problem involved too many variables.

He overcame the difficulty brilliantly, by considering a "circular" process, or cycle, in which the working substance first does some work and then returns to the initial state (using for this a fraction of the work done previously). Each element of the heat engine (including the working substance) is thus in the same state at the start and end of the cycle so that we find the "net result" after each separate cycle because every cycle is identical to the one that precedes it.

Let us analyze such a cycle. Carnot considered an ideal engine such that he only needed to know whether it had a cylinder and a piston (or a turbine) that was driven by the expanding working substance, for instance, a gas. The temperature of the gas may vary: the gas may be heated up by a special system, the hot body, and cooled by another system, the heat sink. In addition, it is natural to assume (and this is what makes the engine "ideal") that neither heat nor work disappear, i.e. heat is not radiated away to the ambient, and work is not spent to overcome friction.

In order to describe what happens to the gas, one has to know how its volume $V$, pressure $p$, and temperature $T$ are changed. If the temperature of the gas remains constant, the process is said to be isothermal; if the pressure remains constant, the process is isobaric; and if the volume is kept constant, the process is isochoric. Clearly, any number of processes can be devised in which all three characteristics $p$, $V$, $T$ change simultaneously. The Carnot cycle uses a process of just this type, the so-called adiabatic, or isentropic, process. In an adiabatic process the gas neither gains heat from the outside nor loses it to the ambient. None of the three variables $p$, $V$, or $T$ remains constant in this process.

We shall illustrate the states of the gas in the cycle by a graph whose axes indicate the pressure and volume of the gas. We are dealing with an ideal gas so the graph can be plotted by knowing only Boyle's and Gay-Lussac's laws (Charles' law). We assume that these laws are well known and that the reader even was taught how these two are merged into the Clapeyron-Mendeleev law (the gas equation) for one mole:

$$pV = RT$$

where $T = t + 273.15$ is the temperature in degrees Kelvin, and $t$ is the temperature in degrees Celsius.

Recall that segments of curves on graphs are called isotherms ($T$ = const), isobars ($p$ = const), or isochors ($V$ = const), similarly. A segment of a curve describing an adiabatic process is called an adiabat. We shall not explain in detail how to plot the curves for an ideal gas and shall move directly to our main subject.

In order to describe the Carnot cycle, we use an illustrative (but by no means real) experiment.

Imagine three units. The first of them is a stove, and a cylinder containing a gas placed on this stove is heated to a temperature $T_1$. The second is a thermos such that the same cylinder with the gas put into this unit neither loses nor acquires heat. And finally, the third unit is the heat sink such that the cylinder with the gas placed in this unit is cooled to a temperature $T_2 < T_1$.

We insert a piston into the cylinder with the gas and move the cylinder from one unit to another. To simplify the argument, we will ignore atmospheric pressure by assuming it to be small compared to the gas pressure under the piston or by assuming that the system is placed *in vacuo*. If the piston is left free under such conditions, the gas under it will start expanding.

Let us organize a process consisting of four stages. Let the gas be initially at a temperature $T_1$.

I. First put the cylinder on the stove and let the gas inside it expand. Wait until the gas does a certain amount of work $A_1$. Since this work is being done at constant temperature, the graph of this stage is the isotherm *ab* (Fig. 5). When the gas expands, it withdraws heat from the hot body. We denote the heat supplied to the gas at this stage by $Q_1$. (Carnot assumed that the work was done by a "downflow" of caloric.)

II. Move the cylinder into the thermos and let the gas continue the expansion, doing an additional work $A_1'$. Since nothing supplies heat to the gas within the thermos, doing work means the gas must cool. Let the gas cool down to a temperature $T_2$. On the graph this process is plotted by the adiabat *bc*, which is steeper than the isotherm *ab* (Fig. 6). In the figure the thermos is simply represented by a table on which the cylinder is neither heated nor cooled.

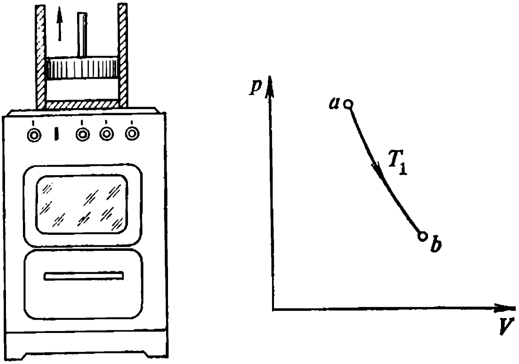

Fig. 5. Carnot cycle: stage I.

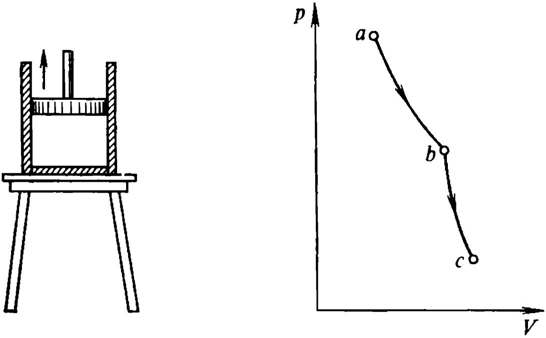

Fig. 6. Carnot cycle: stage II.

III. Now that the temperature of the gas is equal to that of the heat sink, move the cylinder into the heat sink and start compressing the gas, watching that at all times its temperature is constant and equal to $T_2$. This will consume a work

$A_2$ and transfer a heat $Q_2$ to the heat sink. Stop the compression when the pressure and volume of the gas correspond to the third vertex of the curvilinear quadrangle (Fig. 7).

IV Move the cylinder back into the thermos and, continuing to compress the gas, make it return to the initial state, that is, make it reach the pressure and temperature it had at the start of the first stage (Fig. 8). Of course, this means that the pressure and volume at the end of the third stage must be chosen correctly, otherwise we will miss the initial point. These characteristics are easily calculated in advance since the laws for an ideal gas are known. A certain work $A_2'$ also has to be done at the stage *da*.

As a result of the four stages, the working substance should not change state, the hot body lose the amount of heat $Q_1$, and the heat sink gain the heat $Q_2$. The amount of heat $Q_1 - Q_2$ is spent doing useful work.

So far the message of our analysis was that a heat engine cannot utilize all the heat transferred from the hot body, that some heat must be transferred to the heat sink.

Carnot proved that the fraction of the utilized heat, $(Q_1 - Q_2)/Q_1$, only depends on the temperatures $T_1$ and $T_2$, and is independent of all other factors including the properties of the working substance.

The proof of this theorem is one of the most elegant in physics. What surprises us in Carnot's discovery is that he did not know the law of the conservation of energy when he wrote his memoir. For him the transfer of heat was the "downflow" of caloric. Moreover, by using the experimental

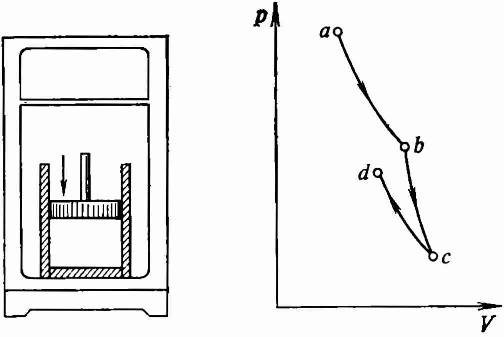

Fig. Carnot cycle: stage III.

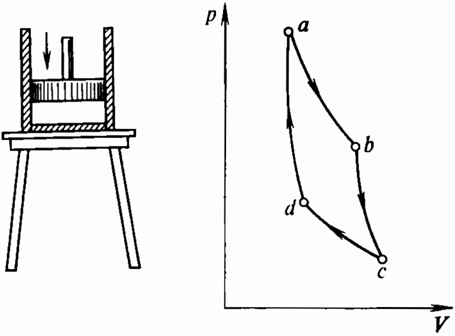

Fig. 8. Carnot cycle: stage IV.

data on the change in gases' heat capacity, accompanying its change in density, Carnot concluded that "the downflow of caloric produces more driving force at lower temperatures than at higher". In Carnot's terminology, the driving force is the work done by an engine per cycle; hence, the title of the memoir.

## Carnot's Great Theorem

If, instead of our thought-experiment, all the operations had been carried out in "live" conditions, we would have found that some heat was spent to heat up the walls of the cylinder, to produce irregularities in the piston's motion, and so on. "Adverse" losses become larger, the greater the difference between the gas and the ambient, and the greater the piston's velocity. We assume, therefore, that the piston moves very slowly and that the temperature difference between the gas and, for example, the hot body is very small. Obviously, these assumptions cannot hold for real heat engines because otherwise an engine would work infinitely slowly and its power would be infinitesimal.

But, following Carnot, we are looking for the conditions that will maximize the useful work and thus we have to resign ourselves to the fact that this work is done by an engine with zero power.

It is immediately evident that all the operations in the cycle (there are only four of them) can be arranged in the reverse order because losses are absent. If the stages are denoted by the letters $\alpha$, $\beta$, $\gamma$, $\delta$, the Carnot cycle can be written in the form $C = \delta\gamma\beta\alpha$ (the symbols must be read from right to left).

The reverse operations are denoted by the symbols $\alpha^{-1}$, $\beta^{-1}$, $\gamma^{-1}$, $\delta^{-1}$. Thus, the operation $\alpha$ corresponds to the motion along the isotherm from the point $a$ to $b$, and $\alpha^{-1}$ corresponds to the reverse motion from $b$ to $a$. After two consecutive operations $\alpha$ and $\alpha^{-1}$ the gas has obviously returned to the initial state. We use the following notation to indicate this: $\alpha^{-1}\alpha = 1$.

The cycle $C$ in the ideal case can therefore proceed in reverse order. This reverse cycle is denoted by $C^{-1} = \alpha^{-1}\beta^{-1}\gamma^{-1}\delta^{-1}$. Obviously,

$$C^{-1}C = \alpha^{-1}\beta^{-1}\gamma^{-1}\delta^{-1}\delta\gamma\beta\alpha = 1$$

This notation simply means that after performing a cycle $C$ and then a cycle $C^{-1}$ we return the system to its initial state: the hot body receives back the amount of heat $Q_1$, the amount $Q_2$ is widhdrawn from the heat sink, and these operations will consume all the work gained in the forward cycle.

In order to return the system (the hot body, heat sink, and working gas) to the initial state, it is not mandatory to use a cycle $C^{-1}$ (the reverse of cycle $C$). We can employ any other reversible cycle, call it $D$. A composition of two cycles $CD^{-1}$ or $DC^{-1}$ returns all the elements of the system to their initial states while each of the cycles $C$ or $D$ (or $C^{-1}$ or $D^{-1}$) returns only the working gas to the initial state. After each of these cycles has been completed, work is done (or consumed) and heat is transferred from the hot body to the heat sink (or in the reverse direction).

A question that immediately arises is whether any reversible cycle that can be performed with the given temperatures of the hot body and heat sink is equivalent to the cycle $C$. In other words, whether in an arbitrary cycle the heat withdrawn from the hot body is $Q_1$ and the heat transferred to the heat sink is $Q_2$ (the amount of work determines the difference $Q_1 - Q_2$ (this is the energy conservation law), but the quantities $Q_1$ and $Q_2$ could be different). Otherwise the system will not be returned to the initial state. If this condition is not satisfied, we have consumed in the new cycle all of the work gained in the cycle $C$ but because the system has not returned to the initial state some of the heat has been transferred from the hot body to the heat sink or from the heat sink to the hot body without doing (or consuming) any work and without any change in the surrounding medium. The problem can be posed thus: Does the combination of any two cycles always give $CD^{-1} = 1$ for cycle $D$?

The problem is solved by Carnot's theorem which in fact states that every reversible cycle must have the same efficiency, that is, the ratio $Q_2/Q_1$ must be the same and equal to that of the Carnot cycle.

This statement can be proved very easily. In fact, the proof is contained by the above words. If the system does not return to the initial state after the two cycles, $CD^{-1}$, and the heat sink receives less heat in cycle $C$ than it yields in cycle $D^{-1}$, as a result of the two cycles the content of heat in the heat sink is diminished and that in the hot body is increased. In nature, however, no process is possible without the heat being transferred from a hot to a cold body changing some other part of the system. Hence, the process is impossible.

If some heat passes from the hot body to the heat sink as a result of the sequence $CD^{-1}$, consider another sequence with the direct cycle $D$ and reverse cycle $C^{-1}$. The two cycles $DC^{-1}$ again cool the heat sink and heat up the hot body.

Of course, Carnot's original arguments were different (he did not use the notion of energy) so we outlined the modern line of reasoning. But the theorem is due to Carnot and states that the maximum work obtainable from a reversible cycle is determined only by the temperatures of the hot body and the heat sink, and is independent of both the properties of the working substance and any design features of the heat engine. With given temperatures of the hot body and the heat sink, all reversible cycles have the same efficiency, i.e. they convert the same fraction of heat obtained from the hot body into work, as the Carnot cycle.

Note that if the engines are not ideal or if their work is not reversible, the situation only deteriorates because of additional losses.

Carnot therefore was able to establish a theoretical limit for the work obtainable from a heat engine.

Carnot was unable to derive a formula for this work and thus his work was not completed.

We shall conclude this story of Carnot with the words in which he put his law: "The driving force of heat is independent of the agents chosen to produce it; its amount is solely determined by the temperatures of bodies between which, in the long run, the caloric is transferred."

## Carnot's Line of Reasoning

The arguments we used to arrive at Carnot's theorem are clear and conclusive, but Carnot could not reason in this way. He did not know that the work done by a heat engine is equal, if there are no losses, to the difference between the amount of heat obtained by the working gas from the heater and the amount of heat transferred to the heat sink. The simple formula

$$\text{work} = Q_2 - Q_1$$

was unknown to him. For Carnot, work was produced by caloric falling from a higher to a lower level. Note that all the caloric is transferred to the heat sink, just as all the water at a hydroelectric power station escapes from the dam. Nonetheless, Carnot came to the correct result and, from his standpoint, proved his theorem.

If there were a heat engine more efficient than the Carnot cycle, it would produce more energy. This means that it would spend less energy "lifting" the caloric back to the "higher" level, returning it to the hot body. Hence, work would be done without changing the content of caloric in the hot body, and Carnot realized that this is impossible. In the language of today, this contradicts the law of the conservation of energy.

Similar arguments can be used to "prove" that there cannot be a reversible cycle with an efficiency lower than that of the Carnot cycle. It is sufficient to use the less efficient cycle for transferring caloric from the hot body to the heat sink and to return it by the Carnot cycle. It will again result in a work appearing "from nowhere".

An almost complete analogy with a dam is evident. The work obtainable in an ideal hydroelectric power station (zero losses) is determined only by the water head (the difference between the upstream and downstream water levels). But we know what the level of water is and are able to measure it; as for the level of caloric, it left the stage without ever having been estimated. Carnot's theorem is not based on the impossibility of an "ordinary" perpetual motion machine but on the impossibility of heat transfer from a cold to a hot body. This would create a perpetual motion machine of the second kind, which could work by freezing its surroundings. This engine would solve any energy crisis beautifully, were it not forbidden by nature. We can see that Carnot made a serious mistake, but his result ultimately proved correct. The intuition of a scientist sometimes enables him to arrive at a correct conclusion despite faulty arguments. No wonder Carnot's contemporaries failed to do credit to his spectacular achievement.

He could be understood only by those who accepted the caloric model but the model was clearly passing out of contention even in Carnot's time.

## A Simple Problem

Let us pass awhile in order to give an example of a very simple irreversible process that had misguided some people.

The heating of a room in a well-managed household is controlled by turning a knob. The *Hand-*

*book of Useful Hints* advises people not to switch the heating off for the night because all the energy economized by this operation will be spent in the morning to heat the room back up to the former level. As if there were a conservation law: the amount lost must be compensated by the same amount returned.

It is rather difficult to evaluate how conclusive these arguments sound, but it is simple to show that they are wrong.

Where does the heat from the room go? It flows across the walls to the street, to the landing, even into a neighbor's apartment if he is out and the heating is off.

The flow of heat is governed by a law discovered by Newton. The amount of heat lost from the room per unit time across a unit surface area is proportional to the temperature difference between the two sides of the wall:

$$Q = k\,(T - T_0) = k\,\Delta T$$

where $T$ is the temperature in the room, $T_0$ is the temperature in the street, and $k$ is the coefficient characterizing the thermal conduction of the wall and the contiguous layers of air.

This flux $Q$ is the only source of the losses replenished by the energy spent by the heating device. The longer the time $Q$ is small, the less the energy consumed.

All other details are irrelevant, the only factor is the mean temperature difference during 24 hours. The lower this difference, and hence, the lower the mean room temperature during this time, the more the energy economized (this example was given by Albert Allen Bartlett in his lecture when he received the Millikan Medal in 1981. This prize is awarded to teachers in the USA).

## The Law of the Conservation of Energy

Caloric must be conserved; work is done due to a "downflow" of caloric from a higher to a lower level. This idea was generally accepted at the beginning of the last century and Carnot certainly shared it when he was writing his memoir. The role of potential energy in this theory was attributed to temperature and had the physicists had better understanding of mechanics they would have been worried that the caloric had nothing resembling kinetic energy.

The situation with heat was even more complicated since physicists had no proper understanding of energy. The term "energy" appeared at the beginning of the 19th century having been introduced into mechanics by Thomas Young. It is probably not surprising that conversion and conservation of energy were not discovered by a physicist but by a physician, Mayer.

In 1840 Mayer went to the island of Java as a ship's doctor. Two notes from his diary, which was written very regularly, have survived. One of them is a record of his talk with a navigator who told him that during a storm the water in the ocean get warmer and was probably the first step to his discovery. The other concerns a fact he had noticed while he was letting blood from sailors with pneumonia (this method was often practiced in medicine at that time). Mayer's attention was drawn to a fact that had been known to the local doctors for a long time though it had never surprised them. The venous blood of sailors was not dark, the colour European physicians were used to. It was bright-red. Mayer found an unexpected explanation. A human being resembles a heat engine. The heat released in his body is a result of combustion, that is, oxidation processes in human blood. The animal heat described and discussed by scientists does not differ in essence from any other heat. It requires fuel to be produced and the combustion waste, namely, carbon dioxide, is transported by blood back to the lungs. The blood filled with a "smoke", i.e. the combustion products, becomes dark. In a hot climate a small amount of heat is needed, the consumption of the fuel is lower, the combustion is not so intensive, and so the blood remains quite bright.

The principal assumption in this picture was that the heat released occurred as a result of a chemical reaction. The idea was simple but almost unacceptable in Europe at that time. Even Mayer's note concerning the water warmed during a storm was not accepted by the learned professors in Tübingen to whom he turned for support.

The paper he sent to Poggendorff's journal (we have already mentioned it) in July 1841 was ignored by the editor and its receipt was not even acknowledged. True, the ideas expressed there were presented not very clearly: it was written by a physician who had never dealt with physics. The paper was described as: "On Quantitative and Qualitative Evaluation of Force. A work by

J.R. Mayer, doctor of medicine and surgery, practicing physician in Heilbronn"

A year later Mayer published a new work in a chemical journal, supported by calculations. This time the help came from a famous physiologist Baron Justus von Liebig.

It was only in 1845 that Mayer managed to publish a detailed work, "Organic Motion and Its Relation to Metabolism" (obvioulsy the title was again not very attractive to physicists).

In the meantime Mayer had not only come to understand that energy is converted from one state into another, but using Gay-Lussac's experiments, he also found the mechanical equivalent of heat, his estimate being 365 kgf·m per large calorie (3.7 ergs per calorie).

Mayer's results seemed equally strange to biologists. Many biologists (called vitalists) believed some special vital force was the source of the activity of a living organism, although our current understanding of the close relationship between biology and physics was initiated by Mayer's discovery. Mayer's fate was tragic. He was hounded by his learned colleagues and was not even appreciated by his relatives. He spent ten years in a lunatic asylum and recognition only came to him in 1878, several years before his death.

At the same time that Mayer was trying in vain to persuade the learned societies of the validity of his ideas concerning the conversion of energy into heat, similar ideas were being developed by James Prescott Joule in England.

Joule's first work dates from 1841. It dealt with a study of the heat released from conductors when current was passed through them. It is of interest that it was the same year in which Mayer first calculated the thermal equivalent of work. He had written to his friend Karl Josef von Bauer about it, but published his results later.

From the experiments Joule concluded that the release of heat occurred due to the battery's work and as a result of the chemical reactions taking place in it. Having started from this, Joule discovered what we call Joule's law.

Joule strengthened his confidence in the nature of heat by other experiments and, like Mayer, he found the mechanical equivalent of heat. Such experiments had been carried out by Joule for many years and they all proved that heat appeared as a result of work. Thus it was finally shown that the theory of nondestructible caloric was incorrect and should be forgotten.

Joule, too, was not immediately recognized by his contemporaries. The influence of the old theories based upon the belief in authorities was too strong and hindered the acceptance of new concepts about the equivalence of heat and work. But numerous new experiments carried out under various conditions confirmed these ideas. Liebig did not forget what he had learnt from Mayer, and in his work "On Animal Heat" he resolutely supported the conclusion that all the heat in a living organism appears due to the combustion of food.

Hermann Ludwig Ferdinand von Helmholtz developed his ideas about "conservation of force" (i.e. energy) in 1847 (but he failed to recognize Mayer's contribution in time).

Thus, in the 1840's the efforts of many naturalists led to a formulation of, probably, the most important law of nature: the law of the conservation of energy. It is also called the first law of thermodynamics.

It is interesting that one more difficulty was encountered on the way to accepting this law. It was possible to concede eventually that energy could not appear out of nothing and that it was impossible to construct a perpetual motion machine, but it was difficult to realize that energy could not vanish. The work of a horse is wasted through the friction in cart wheels, the heat of a furnace is dissipated irrevocably throughout the room. At every step we can see how energy disappears and how work is wasted to no purpose, but state, nevertheless, that energy is conserved. The paradox was solved only when it was realized that heat was related to molecular motion and that the "vanished energy" was converted into the energy of this motion.

At this point let us return to Carnot. Neither Mayer nor Joule had thought of him. The explanation of the law of the conservation of energy and Carnot's principle was completed by Clausius. His work was published in 1850 by Poggendorff. Clausius was the first to speak of the equivalence of heat and work as of the first law of a theory of heat. He also arrived at the equation which Carnot had failed to derive. It called for a simple thing to have been mentioned: every body possesses internal energy which can be increased by work being done on the body and by heat being supplied to it. The significance of this statement lies in the conjunction "and". What it says can be written as a formula:

$$\Delta U = \Delta Q + \Delta A$$

This simple formula has a profound meaning. In mechanics the energy of a body increases when some external forces do some work on this body. This statement can be written as follows: $\Delta U = \Delta A$, implying, for example, that $\Delta A$ is the work of compression of a spring, and $\Delta U$ is the increase in its potential energy. But compression is not the only way of increasing the energy of a spring, it will be increased by heating, too. By supplying heat to a system, we also increase its energy.

It is very important to understand that the final state of a system cannot reveal which factor made the system increase its energy, heat or work. Clausius himself called $U$ "the heat contained in a body" contrasting it to $Q$, "the heat supplied to a body" Now $U$ is called internal energy (or simply energy), and $\Delta U$ is its increment.

As we said earlier, the energy $U$ of a body can be changed both by supplying heat to it and by doing work on it, but these contributions, so to say, become depersonalized by turning into a unified physical quantity which is the energy $U$. Clausius established the concept of energy (to be more exact, internal energy) in the science of thermal phenomena. He borrowed the term from mechanics: "As for terms, I regard as the most suitable the word "energy" used by Thomson, because the quantity, which is referred to here fully corresponds to the quantity denoted by this term in mathematics... ." Other physicists suggested the terms "internal heat", "internal work", or "the action function" No quantity can be called the heat $Q$ of a body, as there is no quantity inside a body which can be called the work $A$. A state with an energy $U$ can be obtained in different ways, each time choosing different quantities of the heat supplied and the work done, whilst maintaining the constancy of their sum. It was this principal "stratagem" of nature which made its understanding so long and hard.

Now we can finish the story about the Carnot cycle and obtain the formula for the efficiency of a heat engine. But to do this, we need to know a formula for the work done by a gas (it will suffice to use the formulas for an ideal gas because Carnot cycle calculations are independent of the choice of a working substance).

The work required to compress one mole of an ideal gas from a volume $V_0$ to a volume $V$ at a constant temperature is

$$A = -RT \ln \frac{V}{V_0}$$

(ln is the natural logarithm. If $y = \ln x$, then $x = e^y$, and $\log x = \ln x \cdot \log e \cong 0.23 \ln x$).

If $V_0 < V$ (the gas expands), then $A > 0$ and the gas has done some work.

This formula is derived as follows.

The state of an ideal gas, as we know, satisfies the Clapeyron-Mendeleev equation of state

$$pV = RT$$

(we shall always assume that we are operating with exactly one mole of a gas).

Let the gas be in a container with a piston and let us apply a pressure $p$ to the piston. The piston will compress the gas and do some work. If the piston's area is $\sigma$, the force applied to the piston is $p\sigma$. If this force is constant and the displace-

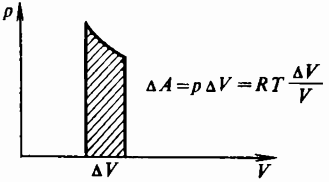

Fig. 9. Isothermal compression of gas.

ment of the piston is $\Delta l$, the force does the work $\Delta A = p\sigma\,\Delta l$. It is easy to see that the product $\sigma\,\Delta l$ is simply a decrease in the gas's volume, $-\Delta V$ We used the negative sign to make $\Delta A$ positive. Hence, the expression for the work done on the gas is (Fig. 9)

$$\Delta A = -p\,\Delta V \quad (\Delta A > 0 \text{ if } \Delta V < 0)$$

Using the equation of an ideal gas, we can eliminate $p$:

$$\Delta A = -\frac{RT}{V}\,\Delta V$$

or

$$\Delta V = -\frac{V}{RT}\,\Delta A$$

This is the equation we have to solve.

Let the gas be compressed from a volume $V$ to a volume, for example, $\frac{1}{2}V$ $\left(\text{i.e. } \Delta V = \frac{1}{2}V\right)$. Repeat this operation 10 times. After each successive stage the volume becomes $\frac{1}{2}V$, $\frac{1}{4}V$, $\frac{1}{8}V$, $\frac{1}{2^{10}}V$. By virtue of the derived equation we see that to decrease the volume from $V$ to $\frac{1}{2}V$ the work should be approximately equal to

$$\Delta A=\frac{2}{3}RT \quad \left(\text{stage 1: } V\to\frac{1}{2}V\right)$$

Instead of taking into account the exact change in the volume on the right-hand side, we substitute $V$ by the average $\frac{1}{2}\left(V+\frac{1}{2}V\right)=\frac{3}{4}V$ of the values of volume at the beginning and end of the stage. It is clear that reducing the stages and thereby decreasing the change in the volumes, we can make the error of this approximation arbitrarily small.

Let us calculate the work done on the gas at the second stage in the same way. Here we again substitute the volume by the average $\frac{1}{2}\left(\frac{1}{2}V+\frac{1}{4}V\right)=$ $=\frac{3}{8}V$. To decrease the volume again by a factor of 2, we should set $\Delta V=\frac{1}{4}V$ and obtain

$$\Delta A=\frac{2}{3}RT \quad \left(\text{stage 2: } \frac{1}{2}V\to\frac{1}{4}V\right)$$

Now it is not difficult to deduce that at each stage the reduction of the volume by a factor of 2 results in the same work

$$\Delta A=\frac{2}{3}RT$$

The work done will thus increase in an arithmetic progression while the volume will decrease in a geometric progression.

We can write now similar formulas for the case when an initial volume $V_0$ is reduced at each stage by a very small fraction $\frac{1}{n}V$, $n\gg 1$. In this case after $N$ stages ($N \gg 1$) the ratio of volumes is

$$\frac{V}{V_0} = \left(1 - \frac{1}{n}\right)^N$$

and the work done is

$$A = N \frac{1}{n} RT$$

Eliminating the $N$ from these formulas, we obtain the relation between the change in the volume $V/V_0$ and the work $A$:

$$\frac{V}{V_0} = \left[\left(1 - \frac{1}{n}\right)^n\right]^{A/RT}$$

If now $n$ tends to infinity, $n \to \infty$, the expression in the brackets is known to tend to $\frac{1}{e} = \frac{1}{2.7172\ldots}$:

$$\lim_{n \to \infty} \left(1 - \frac{1}{n}\right)^n = \frac{1}{\lim\limits_{n \to \infty} \left(1 + \frac{1}{n}\right)^n} = \frac{1}{e}$$

Therefore,

$$\frac{V}{V_0} = e^{-A/RT}$$

or

$$A = -RT \ln \frac{V}{V_0}$$

It is useful to give a geometric illustration of the obtained formula. Let us plot the function $p(V, T)$ at constant $T$ (Fig. 10); it is a hyperbola

$$p = \frac{RT}{V}$$

When a volume $V$ changes by $\Delta V$, the work $A$ is given by the area of the hatched band, and the

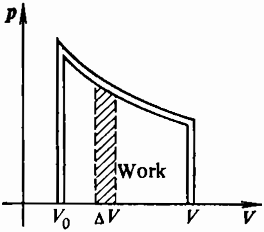

Fig. 10. Work done during isothermal compression.

total work needed to compress the gas from a volume $V_0$ to a volume $V$ is obviously equal to the area under the segment of the hyperbola traced by the double curve.

## Adiabats

Now we should study in more detail the behavior of the gas in the thermos, when no heat is supplied to or removed from the gas. The temperature of the gas then changes only at the expense of its internal energy.

If the gas-filled container is thermally insulated, the work done on the gas or the work done by the gas is the only factor changing its internal energy:

$$\Delta U = \Delta A = -p\,\Delta V = -\frac{RT}{V}\,\Delta V$$

If the gas were heated at constant volume, the change in the energy would only depend on the heat supplied to the body. Then the following formula would hold for the energy:

$$\Delta U = c_V\,\Delta T$$

where $c_V$ is the heat capacity of the gas (per mole) at constant volume. This formula is simply the definition of $c_V$. The two formulas above reflect the fact that a change in the internal energy can happen in two ways: owing to heat or owing to work. Consequently, $\Delta U$ can be calculated by replacing the adiabatic process by another consisting of two stages. First we change temperature at constant volume, then $U$ is incremented by $c_V\,\Delta T$ After this the gas is allowed to expand at constant $T$. Then the value of $U$ remains constant, and the work done by the gas exactly compensates for the amount of heat spent at the first stage. By equating the $\Delta U$ calculated by the two methods, we obtain

$$\frac{\Delta V}{V}+\frac{c_V}{R}\frac{\Delta T}{T}=0$$

If $c_V$ is independent of both $T$ and $V$ (this is true when the temperature of an ideal gas undergoes only moderate changes), this equation can be resolved. It is very easily verified that

$$VT^{c_V/R}=\text{const}$$

satisfies the equation. This statement can be tested by substituting $V$ and $T$ by the slightly incremented values $V+\Delta V$ and $T+\Delta T$ We find that the constant remains unaltered if we neglect the $(\Delta V)^2$, $(\Delta T)^2$, and $\Delta V\,\Delta T$ terms. If pressure $p$ is introduced instead of $T$, the formula becomes

$$pV^{\gamma}=\text{const}$$

(a different constant, of course), where

$$\gamma=\frac{c_V+R}{c_V}$$

Note also that $R$ is numerically equal to the work done by an ideal gas if its temperature is increased one degree at constant pressure:

$$-\Delta A = p\,\Delta V = R\,\Delta T$$

If the gas is heated not at constant volume but at constant pressure, additional $R$ calories per mole have to be supplied in order to compensate for the loss of energy spent on the expansion of the gas (this was already clear to Carnot).

The quantity $c_V + R$ is called the heat capacity at constant pressure and denoted by $c_p$. Hence,

$$\gamma = \frac{c_p}{c_V}$$

and the relation between the pressure of an ideal gas and its volume in the adiabatic process is

$$pV^{c_p/c_V} = \text{const}$$

This formula is called the adiabat equation. Processes in real gases are approximately described by the formula

$$pV^n = \text{const}$$

where $n$ is a real number. The curve is then called a polytropic compression curve.

## Carnot Function

We already know that Carnot proved that the efficiency of a heat engine depends only on the hot-body and heat-sink temperatures, but he was unable to derive this formula analytically because he did not know the relations derived above. The formula was obtained by Clausius.

Let us return to the Carnot cycle. In this cycle the isotherms for the temperatures $T_1$ and $T_2$ are joined by adiabats; the following two equations can be written for the two adiabats:

$$VT_1^{c_V/R}=a_1, \quad VT_2^{c_V/R}=a_2$$

where $a_1$ and $a_2$ are two different constants. One property of the adiabat is that, if it joins two points corresponding to temperatures $T_1'$ and $T_2'$, the ratio of volumes $V_1'$ and $V_2'$ at these points is

$$\frac{V_1'}{V_2'}=\left(\frac{T_1'}{T_2'}\right)^{R/c_V}$$

and depends only on the ratio of temperatures. By using this property for the pairs of points $(a, d)$ and $(b, c)$ in the Carnot cycle, we conclude that

$$\frac{V_b}{V_c}=\frac{V_a}{V_d}$$

or that the volumes at the end points of two isotherms of the cycle satisfy an important proportion

$$\frac{V_b}{V_a}=\frac{V_c}{V_d}$$

This is the relation that Carnot lacked.

Now we can calculate the work done in an isothermal process. For the first isotherm $ab$ the work done by the gas is

$$|\Delta A_{ab}|=RT_1 \ln\frac{V_b}{V_a}$$

Obviously, this work equals the amount of heat $Q_1$ supplied by the hot body. The work done by the gas on the second isotherm is

$$|\Delta A_{cd}| = RT_2 \ln \frac{V_d}{V_c}$$

In its turn, this work is equal to the amount of heat $Q_2$ transferred to the heat sink.

Now, taking into account the ratio of the volumes, we can write

$$\left|\frac{\Delta A_{ab}}{\Delta A_{cd}}\right| = \frac{T_1}{T_2}$$

or finally,

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

The Carnot function defining the efficiency is usually given by the ratio of the "utilized" heat $Q_1 - Q_2$ to the heat $Q_1$ supplied by the heater. We can thus write

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

This is the famous formula for the efficiency of a heat engine, namely

$$\eta = \frac{T_1 - T_2}{T_1}$$

Expressed in this form, Carnot's formula is of fundamental importance. I remind the reader that Carnot's memoir had had no such formula, it was derived by Clausius. It shows that the fraction of heat that can be converted into work depends on two temperatures: that of the hot body and that of the heat sink. In mechanics we are used to the idea that the kinetic energy of a body can be converted totally into work. This 100% efficiency is impossible for heat. The possible useful work ("driving force of fire", in Carnot's words) is a function of the initial (hot-body) and final (heat-sink) states of the working gas. One has to get used to this notion of work and the concept resulted in the appearance of a new science: thermodynamics.

## Absolute Temperature Scale

There are moments which can be singled out in the progress of physics when a new idea changes all subsequent history. These moments are referred to as Great Discoveries. Each discovery has its predecessors, but a discovery begins an independent life, often independent of the creator, only after the physical idea has been given a precise mathematical embodiment.

Three great ideas which predetermined and made the birth of new physics at the start of the next century unavoidable stand out in the first half of the 19th century. These are the Faraday-Maxwell concept of the field, Mayer's idea of the conversion and conservation of energy, and Carnot's idea of thermodynamics. These ideas came into the world in different degrees of perfection. The brilliance of the mathematical techniques of Maxwell gave birth to an electrodynamics already largely complete. Mayer's idea conquered the world almost without formulas. Carnot proved only one theorem which yielded a simple formula, $\eta = (T_1 - T_2)/T_1$, but this formula signified a whole new science.

Like the creator of the wave theory (Augustin Jean Fresnel) who used the ether model to derive the formulas of wave optics and obtained laws independent of the model, Carnot succeeded in extracting from the caloric model results so general that all future developments in physics could not refute them. Born of Carnot's short memoir, thermodynamics even now appears as a spectacular achievement of the human mind. After Carnot—and this was one of the most important results of his idea—the notion of temperature at last acquired a precise meaning.

Galileo in his time discovered that all bodies fall at the same acceleration regardless of their nature. Newton discovered that the attractive force between bodies is independent of their nature and is only a function of their masses. Carnot's discovery is equally general.

The Carnot theorem was the first rigorous result in the theory of thermal phenomena. All known about heat before that was mostly descriptive. Physicists (and engineers) knew how to describe different thermal processes, how much heat must be spent to heat up different bodies, and how much heat is released by burning fuel. In short, they were able to compare different amounts of heat and measure temperatures by thermometers, but they were completely in the dark about the meaning of these notions.

Mayer and Joule discovered the relation between heat and energy, and Carnot understood how heat was converted into work. The time has come then to understand what temperature is. Temperature and energy looked alike: adding heat increased the temperature of a body, work done by the body decreased its temperature. But this simple relationship exists only when a single body is involved.

A difficulty arises when one compares the thermal behavior of two bodies. We can easily find by comparison which of two bodies is warmer and which is colder, but we cannot "subtract" one degree from one body and heat another body by the same one degree. The heat capacity of different bodies, that is, the amount of heat required to raise the temperature of the body by one degree, is different in different bodies, and furthermore, changes with temperature. It was clear that if two bodies are at the same temperature, it by no means signifies that they contain identical energy.

Temperature was measured by thermometers, by the length of a mercury or alcohol column, or by the volume of a gas in a sealed instrument. Obviously, the two techniques are far from impeccable.

Mercury and alcohol thermometers are completely unsuitable for accurate measurements since both are based on the assumption that the expansion of mercury and alcohol is proportional to the change in temperature; the assumption is evidently approximate. Moreover, testing this approximation again requires that temperature be measured by some other method.

Actually, physicists were very lucky. Measuring temperature by a gas thermometer is a very good method because fortunately gases at low densities behave almost identically. The reader knows from the school textbooks that gases are adequately described by a universal equation of state.

The secret of this luck lies in the fact that almost all the gases encountered in nature become liquid at very low temperatures. In Carnot's time it was generally believed that such gases as oxygen and nitrogen always remained gaseous (they were even called permanent gases). And at temperatures far above the liquefaction stage gases behave like ideal gases.

Consequently, the gas thermometer still serves as the main instrument for the most precise temperature measurements. These measurements are sufficiently complicated in actual conditions, but the main principle is simple and quite clear.

However, even the gas thermometer leaves much to be desired. One is inclined to envy the physicists of the 19th century who worked neither with very low nor with very high temperatures. Nowadays the temperatures achieved in laboratories go as low as below —273 °C, and as high as millions of degrees in thermonuclear fusion facilities.

Obviously, temperature must be defined, at least theoretically, without invoking any of the properties of specific substances, even ideal gases.

But before going on to new ideas, let us spend some time on how the unit of temperature arose.

We already know that it first appeared spuriously: the boiling point of water was assigned the number 100. This choice has had important consequences: a new gas constant $R = 8.3157$ joules//degree appeared in the Clapeyron-Mendeleev law. This numerical value appeared only because the degree had been introduced very long ago, and every change in gases was habitually referred to the accidentally chosen temperature scale. Now it would be more convenient to redefine one degree and to "anchor" it in the equation of the ideal gas. This would only require diminishing the degree by a factor of 8.3157 and assuming that in this "ideal-gas" scale the temperature is

$$\Theta = 8.3157T$$

The Clapeyron-Mendeleev equation then would take the form

$$pV = \Theta$$

with the right-hand side containing no constant factor. But this redefinition is not yet accepted, the constant $R$ survives in science, the degree being determined as before by the conventional Celsius thermometer.

The dimensionality of the constant $R$ is joule/ /degree. By choosing a different unit for the degree we could achieve $R = 1$, as shown above. This means that temperature can be measured in joules, that is, in units of energy. Degrees and calories have something in common: both are measured in ergs. Nevertheless, they are different physical quantities.

## Lord Kelvin's Discovery

The meaning of temperature attracted the attention of William Thomson (later, Lord Kelvin) who found in 1848 that the Carnot theorem yields a simple but very important corollary. Kelvin noticed that if the work done in a Carnot cycle depends only on the hot-body and heat-sink temperatures, it is possible to establish a new temperature scale independent of the properties of the working substance. The Carnot cycle can be regarded as a device which makes it possible to measure the ratio of two temperatures $T_1$ and $T_2$. To achieve this, one has to use the equality

$$\frac{T_1}{T_2}=\frac{Q_1}{Q_2}$$

By measuring the ratio of the amount of heat removed from the hot body to that transferred to the heat sink (or, which is the same, by measuring the ratio of work done during the two isothermal stages of a Carnot cycle), we obtain the ratio of the hot-body and heat-sink temperatures.

Thus, if a Carnot cycle can be organized for two bodies (using one as the hot body and another as the heat sink), we can determine the ratio of temperatures of the two bodies. A temperature scale thus defined is called an absolute temperature scale. For an absolute temperature (as opposed to the ratio of two temperatures) to have a definite number, the magnitude of the temperature at one point on the new absolute scale must be changed, i.e. one numerical value of temperature must be arbitrarily assigned. After this, every other value is determined, in principle, by using Carnot cycles.

Unfortunately, despite the theoretical elegance of a Kelvin scale, the Carnot cycle is hardly feasible in practice. It is difficult to realize a reversible cycle and to suppress all the losses. It is necessary to find another method of measuring temperature.

## Real Temperature Scale

The problem of temperature from the theoretical viewpoint became quite clear after Kelvin's work. However, the practical problem remained, for what principle must be used to construct the scale of a reference thermometer so that actual measurements can be made?

For many years the reference points of the temperature scale were the melting point of ice and the boiling point of water, and the distance between them was divided into 100, each of which was assumed to be one degree. This scale with two reference points was accepted throughout the world.

From the point of view of accuracy of measurement, the scale had a very serious shortcoming. It was necessary to be able to reproduce very accurately all the conditions as the ice melted and the water boiled.

It would be simpler to use a single reference point, for instance, the melting point of ice, and measure temperature by a ratio of pressures which are related to that of temperatures by the equation of state (or by organizing a Carnot cycle, although this possibility is almost always purely theoretical).

The melting point of ice is, of course, not quite suitable as a reference point because it is a function of pressure and in general is not reliably reproducible. As a result, the single reference point used nowadays is the triple point of water. This is the temperature at which all three phases of water (vapor, water, and ice) are in equilibrium. At every temperature there is a definite pressure of water vapor over ice. If the temperature is gradually increased, all three phases will be in equilibrium at the moment the ice starts to melt. This state corresponds to the temperature 0.01 °C. The point 0.01 °C is rather easily reproducible in a laboratory and has been chosen as the reference point for the thermodynamic scale, being set exactly equal to 273.16 K. The conventional zero of the Celsius scale is at 273.15 K.

This number was chosen in order to make temperatures on the new scale practically indistinguishable from the older two-reference-point Celsius scale.

The transition to the new scale with the triple point of water as the only reference point went almost unnoticed. This reform was carried out in 1954, so that now if we are asked: "What is the temperature at which ice melts at normal pressure?" we must answer: "Roughly 273.15 K" or "Roughly 0 °C". But if asked: "What is the temperature of the triple point of water?" we must answer: "Exactly 273.16 K" or "Exactly 0.01 °C" Scientists are now discussing whether to replace the triple point of water by that of gallium (29.7740 °C), since it is more easy and accurately reproducible.

It is interesting to recall that the idea of a scale with a single reference point was suggested as early as 1873 by D. I. Mendeleev who proposed to define one degree as that increment in temperature which causes the pressure of a gas (Mendeleev suggested hydrogen) to increase by 1 kgf/cm². He chose the melting point of ice to be at a pressure of 100 gf/cm². This new degree (called the metric degree at the time) was equal to 0.2728 °C.

Mendeleev's idea was realized (in a somewhat modified form) only after lapse of 70 years and so

Mendeleev's name is thus related to the modern thermometer scale as well.

## International Temperature Scale

A scale with a single reference point is readily put in agreement with the Kelvin-Mendeleev scale that is based on Carnot's theorem. We have already mentioned that a thermodynamic scale (this is the name of the Kelvin-Mendeleev scale) does not change if every value of the temperature is multiplied by the same number. The choice of a reference point removes this uncertainty. If, for example, we assume that water boils at $T_b = 373.15$ degrees, all arbitrariness is removed since the values of temperature cannot be multiplied by arbitrary factors because $T_b$ must remain constant. As usual, theoretically impeccable methods prove unfeasible for everyday use in conventional, nonmetrological laboratories. A thermodynamic scale only can be used in special, perfectly equipped laboratories. Otherwise the so-called IPTS-68 scale (International Practical Temperature Scale enacted in 1968) is used. In this scale the boiling point of water is exactly 100 °C and there are also other reference points, which are rather difficult to reproduce, that are also assigned specific temperatures. Of course, this scale does not completely coincide with a thermodynamic scale because the temperature of these reference points is not absolutely accurate. In the region of the boiling point of water the IPTS-68 and thermodynamic scales diverge by about 0.004-0.005 K. Therefore, the accuracy of measuring temperature in conventional laboratories is several tenths of one percent. Temperature is presumably the least accurate quantity among those encountered daily. Even the most accurate measurements contain an error of $5 \cdot 10^{-3}\%$. The universal gas constant is known to the same accuracy: $R = 8.340 \pm 0.0022$. The same is true for the mechanical equivalent of heat, to only three decimal places known precisely at present, thus 1 calorie = 4.184 ± 0.0026 joules.

Even now high-precision thermal measurements remain among the most difficult to obtain in a physics laboratory.

## Kinetic Theory of Gases

It would be a hopeless, as well as an absolutely unnecessary, task to try and describe the motion of each individual atom in a gas: no instrument could follow all atoms simultaneously. It was already clear by the middle of the 19th century that systems consisting of a very large number of particles must be described in terms of probability theory, averaging the properties of individual atoms over a large number of constituent atoms, instead of determining the properties of separate atoms.

The second half of the 19th century gave birth to a new science, statistical physics, which culminated in the work of Ludwig Eduard Boltzmann and Josiah Willard Gibbs.

However, its first ideas had been conceived earlier. In this connection, we should mention a remarkable story of the British scientist Waterston.

In 1845 Waterston submitted a paper to the Royal Society of London. The paper showed that the pressure exerted by a gas on the container walls could be explained by the impacts of atoms.

Although the very idea of a gas consisting of atoms was not new at the time, few people seriously believed that atoms could move freely between the walls of a container and that the elastic properties of gases can simply be reduced to the classical mechanics of atoms. The Fellows of the Royal Society did not like Waterston's paper and rejected it. Many years later Rayleigh, one of the founding fathers of the theory of vibrations and the theory of sound, in particular, discovered this paper in the archives of the Royal Society and published it in 1892 in *Philosophical Transactions of the Royal Society.*

Among other things Rayleigh noticed that Waterston had been unwise in not mentioning his predecessors in the first paragraphs of the paper. Daniel Bernoulli had discussed the relationship between the pressure of a gas and the square of the velocity at which its particles moved as early as 1727. Had Waterston mentioned his great predecessor, then, as Rayleigh's pointed out, the referee of the Royal Society would not have dared to declare the paper meaningless and unfit even to be read to the Fellows of the Royal Society.

This was a sad event for physics. What had been accomplished by a single man and went unnoticed was rediscovered later through the work of several people, and the final formula was made by Maxwell in 1859.

This story is very instructive. So much effort went into deriving a formula that now appears to be so simple:

$$p=\frac{1}{3}nm\langle v^2\rangle_{\mathrm{m}}$$

Here $p$ is the pressure of a gas, $n$ is the number of molecules per 1 $\mathrm{cm}^3$ (the density of the gas), $m$ is the mass of one molecule, and $\langle v^2\rangle_{\mathrm{m}}$ is the arithmetic mean of the squares of velocity of molecules.

## Collisions in an Ideal Gas

The above formula shows that the pressure of a gas is directly proportional to the number of molecules per unit volume and hence inversely proportional to the volume of the gas:

$$p\propto\frac{1}{V}$$

This is Boyle's law. But since this law describes the behavior of an ideal gas, the formula also holds for an ideal gas.

And what is an ideal gas from the standpoint of the atomic theory? Sometimes it is said that it is a gas consisting of atoms whose diameters are negligibly small, that is, an ideal gas is assumed to consist of material points. But points have zero size and hence do not collide with one another. If this were so, their velocities would not change over time unless changed in collisions with the walls. Let us assume that a cubic container was filled with a gas, and the gas was let in as a jet so that all the molecules were moving perpendicularly to one of the walls, bouncing back in the opposite direction as if from a mirror. The molecules of the gas then would flow back and forth between the two walls without affecting the motion of one another.

The real picture is obviously quite different. There are many molecules in the container and they frequently collide, changing their velocities each time. The velocities of different molecules will become diverse very rapidly (the diversification being the faster, the larger the number of molecules), and thermal equilibrium will be achieved in the container. Thermal equilibrium means that the pressure and temperature will be equalized throughout the container. Of course, we assume that the walls of the container are at the same temperature all the time and that the container is sufficiently small for the change in gravity with height to be negligible within it. The same "distribution of velocities" will be reached in all parts of the container in the state of thermal equilibrium.

The molecules in such a container will fly in complete disorder, with total chaos existing at all points inside the container.

The ultimate arrival of thermal equilibrium is a very important fact but it is difficult to prove it rigorously. Experiments have confirmed that despite the never-ending collisions of randomly moving molecules in the gas, our instruments can only detect a constant pressure and constant temperature.

The most impressive feature is that the state of thermal equilibrium is totally independent of how the molecules collide. If the collisions are infrequent, the equilibrium will be slow to build up, if collisions are frequent, it will be attained quickly. In monatomic gases equilibrium sets in so quickly that in most cases we can ignore how the build-up proceeded. The important fact is that collisions do take place and that the equilibrium is ultimately reached. The type of collision is absolutely immaterial. The gas may be so rarefied that particles do not collide with one another at all, but only with the walls of the container; regardless of this, thermal equilibrium sets in all the same.

But once thermal equilibrium has been reached in the container, further collisions cannot change anything and whether they take place or not, no appreciable effect is produced on the pressure or the temperature of the gas. For this reason, a model in which molecules are infinitesimally small and do not collide with one another is quite adequate to explain thermal equilibrium.

Nevertheless, it is this model of pointlike molecules that do not collide but are in thermal equilibrium that one usually chooses as a model of an ideal gas.

## What Is the Velocity of Molecules?

Different molecules certainly have different velocities. In order to calculate the pressure of a gas, a special assumption has to be made about the velocity distribution of the molecules, that is, the fraction of molecules that have a given velocity has to be defined.

August Karl Krönig believed (1856) that all molecules move at an identical velocity and that each molecule moves in one of three possible directions parallel to the coordinate axes. The same problem had been taken up by Joule before Krönig (but after Waterston) (1851). Joule correctly interpreted the relation between the molecular impacts against the walls and the gas pressure, but failed to derive the required formula. Finally, Clausius obtained (1857) a new formula without dropping the assumption of equal velocities. Maxwell came to the correct conclusion only two years later.

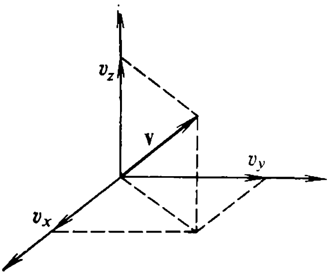

Fig. 11. Three components of velocity.

When a molecule collides with a container wall, the wall receives a certain momentum. Let us begin by assuming that the collision with the wall is elastic. Let the $z$-axis be perpendicular to the wall, and the $x$- and $y$-axes lie in its plane. We decompose the velocity of a molecule into the components along the three axes (Fig. 11). If the impact is elastic, the angle of incidence equals the angle of reflection, so that the velocity components $v_x$ and $v_y$ are unchanged. The component

$v_z$ thereby changes sign. It is thus obvious that the momentum of the molecule is changed by $2mv_z$. Now we have to calculate the number of molecules striking the wall. If the distance between the walls intersecting the $z$-axis is $l$, a particle that hits the wall will arrive at this wall again in a time interval equal to $2l/v_z$, regardless of the other components of its velocity. The number of impacts of this molecule per unit time is then $v_z/2l$.

Each impact transfers a momentum of $2mv_z$ to the wall, so that the momentum transferred per unit time is $mv_z^2/l$.

In order to find the pressure this expression must be summed up over all particles (each particle has its own $v_z$) and divided by the area of the wall, that is, by $l^2$:

$$p = \frac{1}{l^3} \sum mv_z^2 = \frac{Nm}{l^3} \langle v_z^2 \rangle_\mathrm{m}$$

We assume for the sake of simplicity that the container is a cube and its volume is thus $l^3$. Arguments given below show that the pressure must be independent of the container's shape because a gas does not "memorize" the shape.

In this formula we used the definition of the arithmetic mean:

$$\sum v_z^2 = N \langle v_z^2 \rangle_\mathrm{m}$$

where $N$ is the total number of particles.

The last manipulation is the replacement of $\langle v_z^2 \rangle_\mathrm{m}$ by $\frac{1}{3} \langle v^2 \rangle_\mathrm{m}$. Since

$$\langle v^2 \rangle_\mathrm{m} = \langle v_x^2 \rangle_\mathrm{m} + \langle v_y^2 \rangle_\mathrm{m} + \langle v_z^2 \rangle_\mathrm{m}$$

and the terms on the right-hand side are equal (our initial assumption was that the motion is random and no one of the directions in the container is singled out as compared with the other two), we find

$$\langle v^2 \rangle_{\mathrm{m}} = 3 \langle v_z^2 \rangle$$

Replacing now the ratio $N/l^3$ by the density of particles $n$, we arrive at Waterston's formula for pressure.

The problem is evidently not difficult and was correctly solved by Waterston. But Krönig assumed that a molecule hitting the wall transferred all its momentum, and his result was thus twice as small. This would be the case if the molecule did not rebound but adhered to the wall; in the middle of the last century mechanics was still a very complicated science and such mistakes were possible.

The reader might object that the derivation is based on one very important simplification: the impact was assumed elastic. However surprising it might sound, this assumption is unimportant. A molecule may be reflected arbitrarily without affecting the result. The elastic-impact assumption does not change the result, it only makes the derivation much simpler.

The spectacular property of the independence of the final result on the law of reflection follows from the thermal equilibrium between the gas and container walls kept at constant temperature. The ultimate state, that is, thermal equilibrium, does not depend upon how molecules are reflected at the walls.

We shall illustrate this important property of thermal equilibrium by one example. Assume that a light, movable partition is put into the container, separating the gas into two compartments, with the density and temperature of the gas being identical in the two compartments of the container. Assume now that one side of the partition is polished while the other is adhesive, so that the laws of reflection of molecules against the partition are definitely different on both sides. If the pressures exerted on the partition on the two sides proved to be different, the partition would be shifted in order to equalize the pressures. This would mean that the equilibrium density of the gas were different on the two sides of the partition although the pressure and temperature in the two compartments are identical. But this conclusion contradicts the equation of state: pressure and temperature unambiguously determine the density of the gas. Hence, pressure cannot depend on the law of reflection of gas molecules at the walls. These are very general conclusions that are draw from the thermal-equilibrium assumption.

## Kinetic Energy of Molecules and Temperature

Now we have to make the next step and relate molecular impacts and temperature. First we formulate two assumptions which yield Waterston's formula. Following him, we assume that in a gas at thermal equilibrium (i) the molecules of the gas collide only with the walls but not with one another and (ii) the impacts with the walls are elastic. The first assumption signifies that we deal with an ideal gas, and the second, as we have mentioned above, does not change the result while simplifying the derivation.

Now everything is quite simple. If the formula for pressure is rewritten in the form

$$p = \frac{2}{3} n \frac{m \langle v^2 \rangle_{\mathrm{m}}}{2}$$

and we use the Clapeyron-Mendeleev equation

$$p = \frac{1}{V} RT$$

we find

$$RT = \frac{2}{3} \frac{m \langle v^2 \rangle_{\mathrm{m}}}{2} N_{\mathrm{A}}$$

We have replaced the product $nV$ by the Avogadro number $N_{\mathrm{A}}$ because, as is inherent in the Clapeyron-Mendeleev equation, $V$ is the molar volume, and $n$ is the number of particles per cubic cm.

Denoting $R/N_{\mathrm{A}}$ by $k$, we find

$$\frac{m \langle v^2 \rangle_{\mathrm{m}}}{2} = \frac{3}{2} kT$$

The constant $k$ is called Boltzmann's constant and it was introduced by Max Planck in 1899.

The last formula shows that temperature is a measure of the kinetic energy of molecules. If the gas is monatomic, all its energy is the energy of translational motion (the formulas prove to be somewhat more complicated for a gas whose molecules consist of more than one atom).

We can write for one of the components of velocity (e.g. $v_x$)

$$\frac{m\langle v_x^2\rangle_m}{2}=\frac{1}{2}kT$$

Identical formulas can be written for the other two components. The atom is said to have three degrees of freedom, which means that its motion is completely described by the three components of its velocity.

The formulas are such that it appears that each of the three possible perpendicular directions of motion takes up energy equal (on the average) to $\frac{1}{2}kT$ per each molecule. This statement is a particular case of the general law of equipartition which generated many contradictions in the last century.

It is quite surprising that when Waterston addressed the British Association in 1851, he said: "Two gases are in equilibrium in pressure and temperature when each unit of volume contains the same number of atoms and the live force of each atom is also the same." If we note that "live force" was the term for kinetic energy (in contrast to "inanimate force" for what we now call simply force)*, we recognize in this statement a corollary

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* It has already been mentioned that in the 18th century the difference between force and energy was not clearly understood. The "force" contained in a bullet in flight was confused with the force of a wound-up spring. Leibniz introduced the term "live force" to denote kinetic energy and "inanimate force" to denote, for instance, the pressure of a weight on a support. This confusion is noticeable in the term "horsepower", an obsolete unit of power.

of the equipartition law. But again nobody paid attention to Waterston's words.

Waterston's formula related two quantities which his learned opponents considered incomparable since they had absolute different natures. The formula related the energy of the particles with temperature and finally he was reading a physical meaning into the notion of temperature, or at least the temperature of an ideal monatomic gas. Although the author of the formula could not perceive how much it contained, it proved to be the first formula of the incipient kinetic theory of gases.

## Distribution of Energy over Degrees of Freedom

We already know that the energy per each degree of freedom in a monatomic gas is $\frac{1}{2}kT$. In the SI system of units we can choose the degree of the temperature scale so that the energy per degree of freedom changes by half a joule. In this system of units one division of the thermometer scale would correspond to $7 \cdot 10^{22}$ K. This quantity is obviously too large for practical purposes so Kelvin (or Celsius) degrees still reign in physics. Later we shall learn that in nuclear physics and especially in astrophysics the energy temperature scale becomes very convenient. A more practical scale would be obtained by defining a one-degree change in temperature as the change in energy of one degree of freedom of an atom, calculated not per atom but per $N_A$ atoms, that is, by $\frac{1}{2}R$. We have already mentioned this scale and denoted one degree in it by $\Theta$, the energy of one mole of a monatomic gas being given by $\frac{3}{2}\Theta$. However, this scale was never introduced.

If a gas is not monatomic, part of the energy is taken by the vibrations of the atoms inside the molecules and by the rotations of the molecules.

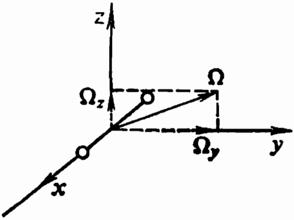

Fig. 12. Rotation of a diatomic molecule.

For example, let us take a two-atom molecule like $O_2$. If oxygen were monatomic, the two atoms would have six degrees of freedom. The number of degrees of freedom could not change when the atoms are joined together to form an $O_2$ molecule because atoms continue to move inside the molecule as well. Such a molecule has three translational and two rotational degrees of freedom (the molecule can rotate around two axes, see Fig. 12)*.

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*For a reason not quite comprehensible in classical physics this molecule does not rotate around its axis, or rather, this degree of freedom has zero energy. We could say that atoms are pointlike and cannot be made to rotate. The situation becomes clear only in quantum mechanics. If a molecule consists of three or more atoms, it

The remaining degree of freedom deals with the vibrations of two atoms with respect to each other. These vibrations are what interests us now.

While translational motion and (it can be proved) each rotational motion are associated with $\frac{1}{2}kT$ of energy, vibrations take $kT$. This is clear if the reader notices that a molecule, like an elastic spring, possesses, in addition to kinetic energy, potential energy which takes exactly one half of the whole. A stringent proof of this statement follows readily from an analysis of the motion of an elastic spring.

The energy of an $O_2$ molecule is thus

$$\frac{3}{2}kT+\frac{2}{2}kT+kT=\frac{7}{2}kT$$

that is, the heat capacity of oxygen is $\frac{7}{2}k$ per molecule, or $\frac{7}{2}R$ per mole.

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can rotate around any axis, and it is said that the molecule in this case has three rotational degrees of freedom (Fig. 13).

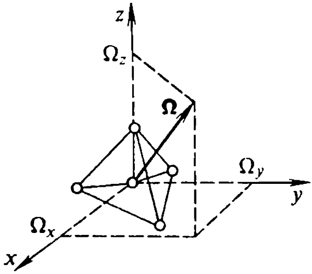


Fig. 13. Rotation of a multiatomic molecule.

The situation is different in a crystal. Particles in solids cannot move freely in space, and can only rotate in specific, complicated crystal structures. Hence, practically all the degrees of freedom belong to vibrations. This means that the molar heat capacity is $3R$ cal/deg, or $1R$ per each vibration (each atom can move in three directions). As $R$ is approximately equal to 2 cal/deg·mol, the heat capacity of all substances in solid state could be expected to be 6 cal/deg, precisely the contention of the Dulong-Petit law. However, experiments show that actual heat capacities diverge from six, and furthermore, depend on temperature. The deviation from the Dulong-Petit value is especially pronounced in the case of carbon.

In the last century this conclusion seemed very strange because it contradicted the equipartition law. The corollaries of the departures from the Dulong-Petit law later proved more serious than would have been expected. They were precursors of the catastrophes that befell classical physics at the end of the century. We shall tell this story later.

## Heat Capacity

We have already noticed that the calorie and the degree have dimensions of energy. The logical conclusion would be that heat capacity is a dimensionless quantity, that is, a quantity independent of what unit is chosen for energy: erg, calorie, or something else. The fact that heat capacity is measured in cal/deg or joule/deg is only due to our habit which prevents degrees being dropped altogether.

What then is measured by heat capacity? Indeed, it has a specific value for each substance, and in addition, depends on temperature.

Let us repeat something already familiar.

The heat capacity of a monatomic ideal gas is simply understood. Each degree of freedom is assigned the energy $\frac{1}{2}kT$. If the heat capacity is referred to an atom rather than to a mole, then (in ergs per degree) it is $\frac{3}{2}k$ and shows the number of degrees of freedom of one atom, that is, the number of dimensions in our three-dimensional space. In the system of units in which $pV = \Theta$ the heat capacity of a monatomic gas would be $\frac{3}{2}$, i.e. one half of the number of degrees of freedom of one atom; this is the meaning hidden in the thermal properties of gases.

But if we deal with the heat capacities of gases with more complex structures or the heat capacities of liquids and crystals, then in the ideal case the heat capacity would define the number of degrees of freedom, with each vibration assigned two degrees of freedom. Actually, the situation is more intriguing. For instance, the electrons producing the electric current in metals take practically no part in thermal motion: their degrees of freedom are "frozen out". Hence, the heat capacity of a solid can be calculated with these electrons completely neglected and with only the vibrations of the heavy nuclei taken into account. This strange phenomenon was understood only with the advent of quantum mechanics.

# Maxwell Distribution

All that was said in the preceding section follows from the fact that a gas, when left undisturbed and under constant conditions (e.g. a gas in a container whose walls are kept at constant temperature), reaches an equilibrium state.

In macroscopic terms, equilibrium means the same temperature, the same pressure, and, if the gas comprises several components (as air does), the same composition of the gas at different points within the container.

Even at equilibrium the molecules in a gas move at random, undergoing collisions among themselves and with the container walls, all the time changing their velocity. However, some characteristics do not vary so randomly. Whatever the change in velocity, the mean square velocity remains constant. This means that if we could follow the motion of one molecule for a sufficiently long period, we would find that periods of acceleration alternate with periods of deceleration, but the square velocity stays the same if averaged over time. The result would be the same if, instead of following one chosen molecule, we measured the velocities of a number of different molecules at one instant of time: the mean value would again be the same (averaged over the ensemble of the molecules). An attentive reader may ask why the result must be the same with these two approaches to measuring the mean velocity. The time average was introduced into physics by Albert Einstein, but it has not yet been rigorously proved even now that the time average is equal to the average over the ensemble of the molecules.

What is the fraction of molecules that move at a given moment of time with a given velocity? This problem was solved by Maxwell, the general theory of statistical properties of physical systems being developed by Boltzmann and Gibbs.

We shall not derive the formula for the Maxwell distribution. What is important for us now is that according to this formula the velocity distribution of molecules is determined by an exponential factor, namely,

$$f(v) \propto \exp\left(-\frac{\varepsilon}{kT}\right)$$

where $mv^2/2 = \varepsilon$ is the kinetic energy of a molecule.

Maxwell published his formula in 1860 at which time the derivation appeared very dubious to his contemporaries. Maxwell was not solving detailed equations for each of the colliding atoms but arrived directly at the conditions of equilibrium in a system consisting of a large number of atoms. But these conditions were not corollaries of mechanics. So it is no surprise that even Thomson tried to verify the distribution formula by analyzing the mechanics of billiard balls. By the way, billiards proved a very popular model for studying the behavior of atoms. The theory of colliding spheres on billiard tables of various shapes grew into an interesting field of mathematics. In 1867 Maxwell returned to the derivation of his formula. In his new paper he proved that the distribution he obtained is indeed not altered by the collisions of molecules. A rigorous derivation of the Maxwell distribution proved far from easy, and some subtle aspects remain to be clarified.

## What Is a Distribution?

At first glance the phrase "The velocity of so many molecules in a gas is, for example, 200 m/s" may not seem strange. But the value 200 cannot be absolutely exact. The number of exact values is infinite; the number of molecules is finite however large it may be. Therefore at each particular moment the molecules cannot have all possible velocities, though this is not needed. Each velocity is measured within a certain accuracy, which actually means that we do not imply the exact velocity 200 m/s but imply a range of velocities from $200 - \delta$ to $200 + \delta$, where $\delta$ is a small value corresponding to experimental conditions.

Without referring to the absolute value of velocity but taking, say, a velocity component $v_x$, one could ask how many molecules (better, what fraction of molecules) have a velocity component that lies in the range $v_x$ to $v_x + \Delta v_x$. This quantity can be expressed as $\Delta n (v_x) = f (v_x) \Delta v_x$. The function $f (v_x)$ is called the distribution function.

In Fig. 14 two graphs are plotted: the stepped curve is an approximate distribution of molecules, and the area of each ($n$th) rectangle (equal to $f_n \Delta v_x$) is the fraction of molecules whose velocities lie in the corresponding range. The interval $\Delta v_x$ is chosen to equal unity. Such graphs are called histograms. If the number of steps of a histogram is very large, then the stepped curve can be replaced with the smooth curve (also traced in Fig. 14). This curve is the distribution function. Since $f(v_x)$ indicates the fraction of molecules, the area under the whole curve must equal unity.

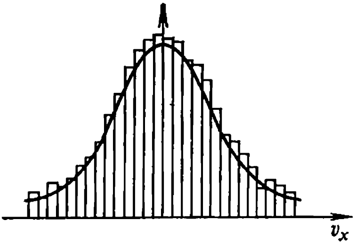


Fig. 14. Histogram and distribution curve (for $v_x$).

Similar graphs, that is, histograms, can be traced for the distribution functions of the other two velocity components, $v_y$ and $v_z$.

Now let us write the expression for the fraction of molecules whose velocity components are $v_x$, $v_y$, and $v_z$ (within certain intervals around these values). This can be done as follows. The fraction of molecules with the velocity component $v_x$ is $f(v_x)\,\Delta v_x$. A certain fraction of these molecules have the second component, $v_y$. This fraction is, obviously,

$$\Delta n(v_x, v_y) = f(v_y)\,f(v_x)\,\Delta v_x\,\Delta v_y$$

Fraction $f(v_z)$ of these molecules will have the third velocity component, $v_z$. Then, the fraction of the total number of molecules whose velocity components are $v_x$, $v_y$, and $v_z$ is

$$\Delta n(v_x, v_y, v_z) = f(v_z) f(v_y) f(v_x) \Delta v_x \Delta v_y \Delta v_z$$

The function

$$f(v_x, v_y, v_z) = f(v_z) f(v_y) f(v_x)$$

can be called the velocity distribution function. These three distribution functions of velocity components are supposed to be identical because in thermal equilibrium all three space orientations are equivalent.

## Various Mean Values

Assuming that the law for the distribution of the velocities for the molecules is known, we can calculate various characteristics of this distribution. The mean velocity equals zero because the negative and positive values of components are equivalent. The calculation of mean values is reduced to the calculation of integrals and cannot be done in a simple way. The mean square velocity is expressed by the already familiar formula:

$$\langle v^2 \rangle_{\mathrm{m}} = \frac{3kT}{2m}$$

or, in case of the mean kinetic energy,

$$\langle E \rangle_{\mathrm{m}} = \frac{3}{2} kT$$

One can also obtain the mean absolute value of velocity:

$$\langle |v| \rangle_{\mathrm{m}} = \left(\frac{8kT}{\pi m}\right)^{1/2} = 1.772 \left(\frac{kT}{m}\right)^{1/2}$$

Finally, velocity of the "most frequently encountered" molecules (the most probable velocity) is

$$\bar{v} = \left(\frac{2kT}{m}\right)^{1/2} = 1.414 \left(\frac{kT}{m}\right)^{1/2}$$

One should not be surprised that molecules with the mean velocity are not the most frequent. The absolute value of velocity is positive, and the number of molecules whose velocity is less than the mean velocity always exceeds the number of molecules whose velocity is higher than the mean velocity. To "compensate" for the molecules having higher velocities, a larger number of molecules having lower velocities is needed. This fact is well known to statisticians. The number of persons whose salary is higher than average is always less than the number of persons whose salary is less than average.

If all the molecules had equal velocities, the three mean values would, certainly, be equal. The difference indicates the spread of velocities.

To characterize the spread of velocities it is convenient to calculate, in addition, the mean square kinetic energy

$$\langle E^2 \rangle_{\mathrm{m}} = \frac{m^2}{4} \langle v^4 \rangle_{\mathrm{m}} = \frac{15}{4} k^2 T^2$$

Now the difference called the variance σ can be calculated:

$$\sigma^2 = \langle E^2\rangle_\mathrm{m} - \langle E\rangle_\mathrm{m}^2 = \frac{3}{2} k^2 T^2$$

We find that temperature reveals another quality: it characterizes the "width", or spread, of the distribution of the velocities (or energies) of the molecules, that is, the natural spread of the kinetic energy of the molecules with respect to the mean.

Thus, the combination of normal distribution and Waterston's formula led to the further development of the concept of temperature as a parameter that determines the spread of energy in the translational motion of gas particles.

## Maxwell Distribution and Chaos

Let us dwell on the Maxwell distribution a little bit more. First of all, when describing a gas, we shall use velocity space instead of coordinate space. This means that we "represent" each molecule by a point whose coordinates are equal to its velocity components. Thus, the origin corresponds to a molecule at rest while the points on the $x$-axis correspond to the molecules moving along this axis with various velocities, etc. This space is illustrated in Fig. 15.

Let us imagine a cube, one of whose vertices is at ($x$, $y$, $z$) and whose edges are parallel to the coordinate axes. Points inside this cube correspond to molecules whose velocity components lie in the ranges bounded by the coordinates of the vertices of the cube. In reality the number of these molecules is continuously changing because the molecules collide, thereby changing their velocities. This will result in the points in the cube "flickering" The disappearance of a point from one cube would mean, then, the appearance of one in another cube (we can easily imagine "velocity space" divided into such cubes).

It is clear that the total number of points, being equal to the total number of gas molecules, remains constant. If we were to describe in detail what happens in each cube, we would not be able to cope with this task. But we are not interested in those details; in fact, they are not needed for we would not know what to do with them. What we are interested in is the mean number of molecules in this cube, and this question is answered by the Maxwell distribution.

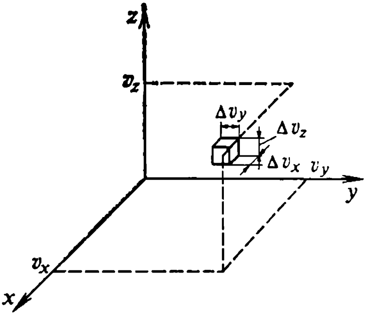


Fig. 15. Cubic unit cell in velocity space.

It can easily be understood that the distribution function can only depend on the square velocities because it must clearly be independent of their orientation. Otherwise a larger number of molecules would move in one direction than in another and the gas would move as a whole.

But we know that this function should decompose into three identical factors, each of which being dependent on only one velocity component (to be more exact, on its square).

Square of velocity equals the sum of squares of components: $v^2 = v_x^2 + v_y^2 + v_z^2$. Thus, it is necessary to find the function of $v^2$ which would decompose into the product of three identical functions of $v_x$, $v_y$, and $v_z$, respectively.

It can be shown that the only function which satisfies this condition is

$$f(v^2) \propto \exp(-\alpha v^2)$$
$$= \exp(-\alpha v_x^2) \exp(-\alpha v_y^2) \exp(-\alpha v_z^2)$$

Further calculations involve integrals and so are omitted. Note only that we calculate the coefficient

$$\alpha = \frac{m}{2kT}$$

assuming that the mean value, e.g. $\langle v_x \rangle^2$ should satisfy the earlier condition $\langle v_x \rangle_m = kT/m$.

We can also write the function which describes the distribution of the kinetic energy of the molecules: it determines the fraction of molecules whose kinetic energy lies in the range $\varepsilon$, $\varepsilon + \Delta\varepsilon$. This function is

$$f(\varepsilon) = (2\pi kT)^{-3/2} \exp\left(-\frac{\varepsilon}{kT}\right) \varepsilon^{1/2}$$

and it is also called the Maxwell distribution function.

The fact that the distribution function decomposes into three factors means that the distributions along all three axes are independent and obey the same law. It can be said that the probability of a molecule appearing in any selected cube (i.e. the probability of a molecule obtaining, as a result of collisions, the velocity corresponding to the coordinates within this cube) decomposes into three factors, that is, into the probabilities for each velocity component to be in the range of values fixed by the corresponding edge of the cube.

This point can be illustrated by the game of dice. Let us throw three dice, each painted a different color. The probability of obtaining a 5, say, on the red die is $\frac{1}{6}$ which is also the probability of throwing a 3 with the green die (or a 4 with the yellow one).

It is fairly obvious that if we cast all three dice simultaneously, the probability of each combination, e.g. 3 (red) + 4 (green) + 1 (yellow) will be equal to the product $\frac{1}{6}\cdot\frac{1}{6}\cdot\frac{1}{6}=\frac{1}{216}$.

The reason for this answer lies in the intuitive certainty that each throw of each die is completely independent of the others and all the triple combinations from 1, 1, 1 to 6, 6, 6 must occur with equal frequency, that is, they all have an equal probability. Of course, the process through which the distribution of the velocities of the molecules is reached as a result of collisions is in no way similar to throwing dice. The latter was only meant to illustrate how a function can decompose into three factors.

The derivation of the Maxwell distribution, although it is not simple, looks so logical that this distribution seems to be the only one possible.

To emphasize how wrong the "obvious" conclusions may be, it is necessary to note that the Maxwell distribution cannot describe a gas in which quantum properties prevail (e.g. electrons in metal, or a photon gas). Quite different assumptions are needed to derive the distribution function for these systems.

A gas in which the molecules obey the Maxwell distribution has a remarkable property, its distribution is time-independent. The velocity of each molecule changes very often (as a result of collisions with other molecules), but the molecule which left a particular cube is replaced with another. If molecules are indistinguishable to us (and this is true!), the distribution of molecules will remain the same all the time.

If we fill a container with a gas, after some time the gas will be in equilibrium, that is, the Maxwell distribution of velocities among the molecules will be reached. This must be independent of the original distribution in the gas because even though its molecules could have had equal velocities or move in some other way, within a certain period the equilibrium distribution is bound to be reached.

On second thought this statement may seem strange and even not quite plausible. We know (and are used to) that in mechanics one has to fix original coordinates and velocities and, using Newton's equations, find the positions and velocities of particles at later (or earlier) moments of time. Here different original data will result in different states of the system. In mechanics, they say, the system "remembers" its original state, that is, in principle, the history of the system can always be reconstructed.

In gases everything occurs in a different way. Whatever the original distribution of velocities, it must finally become the same Maxwell distribution. In this case the system "forgets" its history, and by studying the distribution of a gas in equilibrium one can deduce nothing about its previous state.

The history of a gas filling the container separates into two periods. During the first period the molecules collide with one another and with the walls, and their distribution tends to equilibrium. This period is studied by the special science of nonequilibrium systems. After some hundreds or thousands of collisions of each molecule the system practically reaches the equilibrium state. Subsequent collisions do not affect this state.

If collisions are ignored, that is, if a gas is sufficiently rarefied, we obtain the model of an ideal gas in which collisions are necessary only to attain equilibrium. Even if there are almost no collisions between the molecules, the equilibrium would still be attained through collisions with the walls.

As a result of collisions between molecules the equation of an ideal gas and the Clapeyron-Mendeleev equation are different.

The equilibrium state of the gas discussed above can be described as follows: there is molecular "chaos" in the gas at equilibrium. The term "chaos" implies that the system has not preserved any information about its past.

The concept of "chaos" permits us to simplify the derivation of some formulas. For example, while deriving the formula for the pressure exerted by the gas on the walls of a container, we assumed that the molecules were reflected against the wall. Actually, after colliding with the wall, the molecule, as a rule, sticks to it and remains there for some time; afterwards it breaks away and moves in some direction, having completely "forgotten" the one from which it came. Hence, there is no point in discussing the process of reflection, and it is much simpler to reason as follows: since the properties of the gas are independent of orientation, the momentum transferred by the gas to the wall must be equal to the momentum carried by gas molecules away from the wall.

This must be independent of the peculiarities of the gas interaction with the walls; it relates only to the chaotic motion of the molecules. Should both fluxes (the one towards the wall and the other away from it) be different, that is, should they transfer different momenta, the effect could be detectable at some distance from the wall for the gas would "remember" that it had been reflected from the wall. But this contradicts the hypothesis that the gas is chaotic and has no "memory"

And since the gas does not "remember" about the wall, the result should not depend on the properties of the wall and on the way the atoms are reflected from it. Thus, atoms do not "remember" the shape of a container, and the distribution formula is the same for any container (as has already been mentioned).

Another example of "forgetfulness" is found if a gas is put in a container divided by a partition. If the latter is removed, the gas from both sections mixes, and it is clear that there is no way to distinguish which atom was in which section of the container at the beginning of the experiment.

When a hot teapot is cooling down, it warms the air in the room, but later it is impossible to find what warmed the air. Everybody would agree that one cannot determine the shape of this teapot by measuring temperature in various parts of the room (far from the teapot). This is very much unlike the electromagnetic field: the light reflected from a surface carries information about this surface. A glowing lamp illuminates itself and is clearly visible. We can "see" the teapot using a detector sensitive to infrared waves. But infrared radiation propagates in the form of directional fluxes of electromagnetic waves that warm the detector. The waves emitted by a teapot are not in thermal equilibrium with the air, they are not scattered by its atoms, and therefore they "remember" and can transfer the image of the teapot. By contrast, the chaotic motion of molecules cannot transfer this information.

## Absolute Temperature and Quantum Mechanics

The reference point of the temperature scale is —273.15 °C. This point is called absolute zero. Its meaning became clear only after the kinetic theory of gases related the pressure of a gas to the kinetic energy of its atoms. This theory seemed to indicate that at absolute zero the motion of atoms completely dies out and that the absolute temperature $T$ is merely a measure of the kinetic energy of atoms.

But this explanation, though simple and almost obvious, was incorrect. The electrons in metals move with very high velocities even at $T = 0$. Quantum mechanics has forced on us a completely different approach to the motion of electrons and atoms though it has not complicated the picture. On the contrary, quantum mechanics provides a natural explanation of many concepts, including the concepts of absolute temperature and absolute zero.

However, to follow the story of temperature in terms of quantum mechanics it is necessary to have at least some information about quantum mechanics. Unfortunately, this science cannot be explained in a few words. On the other hand, right now we do not need much. Hence, there is what we shall do: we shall cite some facts without proof but minimize the amount of this information.

If we want to know the behavior of an electron in a magnetic field, quantum mechanics gives the following description.

An electron can be compared to a rotating top (though this comparison is not quite adequate). It is better to say that the electron, like a rotating top, has an intrinsic angular momentum called its spin, without going into the details of rotation. The spin of the electron is related to its intrinsic magnetic moment: an electron in a magnetic field behaves like a magnet.

If an electron is in a constant magnetic field, then, according to the laws of quantum mechanics, its spin can be directed either along the field $\left(\text{and then the projection of the spin on the field direction is } +\frac{1}{2}\hbar\right)$ or against it $\left(\text{and then the projection is } -\frac{1}{2}\hbar\right)$; $\hbar$ is Planck's constant.

The direction of the electron's magnetic moment is opposite to that of the spin; hence, like the spin, it can have two projections on the direction of a magnetic field: the projection is $-\mu_0$ if the spin and the field have the same direction ($\mu_0 > 0$), and $+\mu_0$ if the directions are opposite. The quantity $\mu_0$ is called the Bohr magneton and equals

$$\mu_0 = \frac{e\hbar}{2mc}$$

If the strength of a magnetic field is $H$, the potential energy of an electron in this field is either $\mu_0 H$ (the spin is directed along the field) or $-\mu_0 H$ (the opposite direction of the spin). These arguments finally mean that in a magnetic field an electron can be in one of two states, the energies of these states being $\pm\mu_0 H$. We assume here that the electron has no translational motion, for example, it is bound in an atom.

Using this simple model, many properties related to heat can easily be illustrated.

Let us consider a system consisting of a large number of electrons fixed at various points of space: as an example, we shall take a large number of atoms, each containing electrons. In a magnetic field the energy of this system is determined by the numbers of electrons with different spin directions: along the field and against it.

If we represent the two possible spin directions by two horizontal lines marked with energy values (Fig. 16), the electron spin distribution can be shown by circles, that is, electrons, on these lines (of course, we shall draw only a few circles).

A system of electrons possessing magnetic moments can be compared to an ideal gas, and the

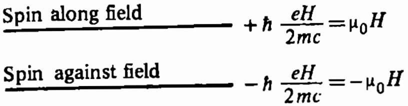


Fig. 16. Energy of an electron in a field.

energy of an electron in a magnetic field plays the role of the velocity (kinetic energy) of atoms. However, kinetic energy can assume any positive value whereas the energy in a magnetic field is allowed to assume only two values.

It is remarkable that this constraint does not change the basic law of statistics, and in a thermal equilibrium the probability of finding a particle in a state with energy $\varepsilon$ is proportional to $\exp(-\varepsilon/kT)$.

As in a gas, it is also necessary that the thermal equilibrium of the atoms be really achievable. Therefore, the magnetic moments must interact (like the atoms in an ideal gas collide). If this condition is satisfied, the law of statistics will be obeyed regardless of the specific mechanism bringing the system to thermal equilibrium.

In this respect our picture of electrons "perched" on two levels illustrates the equilibrium state only, but tells us nothing of how the equilibrium had been reached.

Considering the foregoing discussion, one can conclude that in thermal equilibrium the number of electrons, $n\left(-\frac{1}{2}\right)$, whose energy is $-\mu_0 H$ exceeds the number of electrons, $n\left(+\frac{1}{2}\right)$, whose energy is $\mu_0 H$.

The ratio of these two numbers (referred to as the populations of the levels) is given by the ratio of exponents:

$$n\left(-\frac{1}{2}\right) : n\left(+\frac{1}{2}\right) = \exp\left(\frac{\mu_0 H}{kT}\right) : \exp\left(-\frac{\mu_0 H}{kT}\right)$$

This simple formula has a remarkable property: it is valid for systems consisting of a very large number of particles, and it is almost independent of the detailed structure of the system. The only requirement is that the system has states with only certain energies and that there is a way to reach thermal equilibrium. Then the final equilibrium state of the system will be determined by a single parameter, $T$, that is, its absolute temperature. This property of systems was proved by the American physicist Gibbs at the very beginning of the 20th century.

Until quite recently physicists had not even suspected that there were systems with finite numbers of allowed states. And they never imagined the vast number of wonderful effects that are possible in these simple systems.

## Magnetic Needles

Let us assume that instead of electrons possessing magnetic moments we have a number of randomly scattered compass needles (Fig. 17). Since magnetic needles must point northward, they start swinging with equal amplitude around the south-north direction. Were there no friction in the pivots and no attraction between the needles, the swinging would continue indefinitely. Actually the swinging will ultimately stop because the energy will be dissipated through the friction in the pivots, and all the needles will point northward. Besides, magnetic needles influence one another: their movements are "coupled", that is, they can transfer energy to other needles. One can easily recognize in the behavior of the needles a model of how equilibrium is reached in a system of spins.

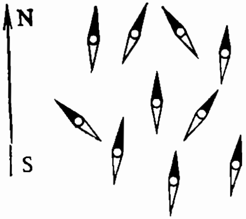


Fig. 17. A system of magnetic needles.

The pivots play the role of a heat sink to which the needles transfer their kinetic energy. Needles at rest resemble the system of spins at $T = 0$. "Zero" temperature appears because the energy is always transferred from the needles to the pivots, and the equilibrium can be reached only after all energy has been transferred.

If we were to study the system of magnetic needles more thoroughly, we would find that the needles do not stop completely but swing with very small amplitudes because of their constant bombardment by air molecules and the minute swaying of the pivots. Thus the energy does not fall off to zero, it stays equal to $kT$ (on the average). This motion is called Brownian movement and theoretical grounds for it were derived by Einstein in 1905.

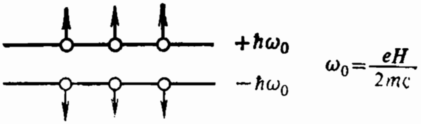


Fig. 18. Equal probabilities of populating energy levels ($T = \infty$).

The model of electrons in a magnetic field (or the model of magnetic needles) is very useful when we try to understand what the absolute zero is.

At any temperature the two possible spin directions will occur with different probabilities. At very low temperatures almost all electrons will populate the lower level, that is, their spins will be directed against the field. The higher level will be almost empty, that is, "depopulated". The higher the temperature, the more "populated" the higher level, and, for example, at very high temperatures ($kT \gg \varepsilon$) both spin projections will have nearly equal probability (Fig. 18).

If the temperature drops, the increasingly large fraction of electrons will have spins directed against the field. If $T = 0$, the spins of all electrons will be directed against the field (Fig. 19).

This state of the system corresponds to the absolute zero of temperature.

In quantum theory the concept of absolute zero is given a very clear-cut meaning. Among all the energy levels of any quantum system there is one level which corresponds to the lowest energy. In the example being considered this state is the state in which the spins of all electrons are directed against the field. At absolute zero the system is in the ground state, hence it cannot transfer energy to any other system merely because there is no lower level to which it could transfer after losing energy.

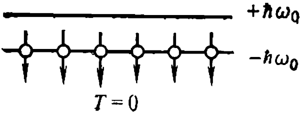


Fig. 19. All the electrons are at the ground level ($T = 0$).

We have already mentioned that the somewhat obscure concept of absolute zero existed long ago because it stemmed from the Gay-Lussac law. But even at the beginning of our century the concept of absolute zero was not completely clear. In *Children's Encyclopaedia*, published in 1914 in Moscow, the following was written: "Thus, in the process of cooling the gas contracts and its volume, consequently, decreases. The question is: Could the volume vanish when the gas is in the state of absolute cold?" These speculations look very naive now, but it is very surprising how much lies hidden in the simple fraction $\frac{1}{266}$ in the original formula obtained by Gay-Lussac.

## Unattainability of Absolute Zero

Everybody knows that the temperature of a body cannot be lowered to exactly absolute zero, although we can approach arbitrarily close to it. This statement reminds us of the well-known paradox about Achilles and a tortoise (called Zeno's paradox). The paradox is as follows: Achilles who runs ten times faster than the tortoise wants to overtake it. Whilst Achilles was running over the distance that initially separated him from the tortoise, the tortoise covered an additional $\frac{1}{10}$ of this distance. Of course, Achilles will quickly cover this distance too, but now the tortoise will have moved $\frac{1}{100}$ farther. And whenever Achilles approached the tortoise, it had invariably moved further forward. Naturally, another approach resolves the problem. The sum $1+\frac{1}{10}+\frac{1}{100}\ldots$ equals $1\frac{1}{9}$ and the paradox is nothing but a statement that an infinitely recurring decimal 1.11... has a finite value.

For Zeno the paradox was that Achilles had to pass an infinite number of segments in a finite time. Zeno did not doubt that Achilles would overtake the tortoise, but he concluded that the segment could not contain an infinite number of parts. The message of Zeno's paradox is much more profound than a mere perplexity at the finite sum of an infinite geometric progression. But even this almost trivial simplicity will be of use in this context.

Let us not argue with Zeno, but modify the problem a little. Assume that the tortoise, being very pedantic, asked that Achilles should make some marks or simply count aloud after covering each stage (each term in the infinite sequence). Since the number of such marks must be infinite, the time of the contest immediately becomes infinitely long.

However fast Achilles marks the stages, he is incapable of making the infinite number of marks. Thus, an innocuous bureaucratic improvement renders a simple task infeasible. In this form Achilles' problem resembles the problem of absolute zero.

In order to cool a body to absolute zero it is necessary to withdraw a finite amount of heat from it. This amount can be easily calculated if we know the relation between the heat capacity of a body and its temperature. But is it possible to drain all the heat a body contains in a single step?

This is where the difficulty lies. Any method of cooling will reduce the temperature by a set factor, but not by a set quantity. When we described the thermodynamic scale, we found that it has a remarkable symmetry. If all temperature values are multiplied by the same factor, the formulas will stay unaltered. This means that to reduce the temperature of a given body from 100 °C to 99 °C and from 200 °C to 198 °C one has to do the same amount of work because $100 : 99 = 200 \quad 198$.

But if all the calculations in thermodynamics contain only the ratios of temperatures, volumes, and so on, then each process used for the purpose of cooling will result in the final (low) temperature being a proportion of the initial (high) temperature, that is, each procedure of temperature reduction can only change the scale, namely, it can decrease the temperature by a certain factor.

Thus, we found in the Carnot cycle that $T_1 : T_2 = Q_1 \quad Q_2$. Obviously, it does not work with either the amount of heat or temperature as such; only their ratio matters.

Now it is easy to understand why an infinite number of steps is needed to reduce the temperature of a body to the absolute zero. Each step is either a closed cycle or a single process, for example, the adiabatic expansion of a cooling gas.

During each step a certain finite amount of work is done and the temperature decreases by some finite factor. Since each step takes a finite time, the total time needed to cool the body to absolute zero is necessarily infinite. In this respect the road to absolute zero resembles the Achilles-and-tortoise stalemate.

One can ask whether the situation is different in the kinetic theory of gases. Could one, say, lower all the spins in the system of electrons to the ground state (for example, by waiting until they radiate away all their excess energy)? But nothing will come of this. Were the system in an infinite, empty space, and the radiated energy gone forever, the spins would certainly lose all their energy and the system would reach a state corresponding to absolute zero. But if the system is enclosed in some volume by walls kept at a constant temperature, then this system will have the temperature of the walls, and it is impossible to lower this temperature without doing some work.

## Entropy

Using a thermometer one can measure the temperature of any body. In fact, the thermometer shows its own temperature, and it is not always easy to find the relation between the readings and the temperature of a body. In everyday life we often refer to the temperature, but usually forget about the complex processes associated with it. Having learnt many years ago how to measure temperature, physicists took a very long time to understand the relationship between temperature and the amount of heat of a body. It was very difficult to guess that there exists a quantity related to temperature, namely, entropy, and that the increment of entropy multiplied by the temperature determines the amount of heat obtained by a body. Entropy was theoretically discovered by Clausius and is one of the most brilliant discoveries among the many for which the 19th century is so famous.

Entropy was introduced into physics theoretically because there is no instrument to measure it. Moreover, there is no method available for comparing the entropies of two different systems, in contrast to what we can do with the temperatures of two bodies.

For example, one cannot take two containers, each filled with a different gas, and say which of them has a higher entropy. The entropy of gases can be found from tables, but there is no instrument, like a barometer or a thermometer, to measure the amount of entropy.

Clausius discovered the concept of entropy while trying to understand the profound meaning of Carnot's investigations. As we already know, Carnot demonstrated that if a reversible thermodynamic process takes place between two "bodies", namely, between a hot body and a heat sink, they form a heat engine which works by withdrawing an amount of heat $|Q_1|$ from the hot body and transferring part of this heat $|Q_2|$ to the heat sink. The amounts of heat $|Q_1|$ and $|Q_2|$ are related to the temperatures $T_1$ and $T_2$, the hot-body and heat-sink temperatures, respectively, thus:

$$|Q_1| \quad |Q_2| = T_1 \quad T_2$$

This relation is valid for any heat engine provided the engine is ideal, that is, it can work "in reverse" and by doing the same work would withdraw $|Q_2|$ from the heat sink and transfer $|Q_1|$ to the hot body.

A more convenient form of the proportion is $Q_1/T_1 = -Q_2/T_2$. The minus sign is the evidence that the heat is withdrawn from the working gas. The result is

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

This expression resembles a conservation law. In a Carnot cycle the quantity $|Q_1|/T_1$ "lost" by the hot body equals the quantity $|Q_2|/T_2$ "gained" by the heat sink.

We know that Carnot worked in terms of the caloric model. This model was to yield a conservation-type relation for a hypothetical heat liquid. The model would be acceptable if a relation like $|Q_1| = |Q_2|$ held in it, for this would mean that heat was conserved and that work was done owing to a heat flow from a higher to a lower level.

If temperature were the analogue of hydraulic head, then the work done by an engine would be proportional to the temperature difference. However, in a reversible process it is not the amount of heat (or caloric) that is considered but another quantity, and the change in this quantity equals the increment of supplied heat divided by the temperature of a body.

The heat participating in the process must be divided by temperature and only then do we obtain the quantity which is conserved in a reversible process.

Let us change our notation and use $\Delta Q_1$ instead of $Q_1$ and $\Delta Q_2$ instead of $Q_2$, emphasizing that we imply the amount of heat $\Delta Q_1$ obtained by the working gas, and the amount of heat $\Delta Q_2$ lost by it. For the Carnot cycle this gives us

$$\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0$$

Clausius postulated that there was a quantity $S$ which, like energy, pressure, and temperature, characterizes the state of a gas. When a small amount of heat $\Delta Q$ is supplied to the gas, $S$ is incremented by

$$\Delta S = \frac{\Delta Q}{T}$$

Clausius gave the quantity $S$ the name "entropy".

After the Clausius' discovery it at last became clear why it had been so difficult to understand the relationship between heat and temperature. It turned out that speaking about the amount of heat contained in a body is meaningless. Heat can be converted into work, can be generated by friction, but in general there is no tendency to conserve heat.

At the same time, the concept of the amount of heat supplied to a body or withdrawn from it has an exact meaning. Heat can be transferred, but is not necessarily conserved. A quantity whose existence had never been suspected turned out to be conserved in a reversible process: it was Clausius' entropy.

Let us see what happens to the entropy of a gas in the Carnot cycle.

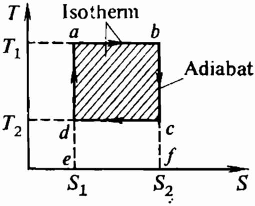
The above relation for the Carnot cycle means that in a Carnot reversible cycle the increase in the entropy of the working gas at the first stage exactly equals the decrease in entropy at the third stage. At the second stage, when the gas is isolated and cannot receive heat, entropy is constant; it is also constant during the fourth stage.

Thus, in a reversible Carnot cycle the entropy of the working gas remains unchanged. It is unchanged in adiabatic processes too.

The concept of entropy can be obtained in a different way, by defining it as a quantity that remains constant in an adiabatic process which is like defining a zero temperature change for an isothermal process. It is very convenient to use entropy for a graphical representation of Carnot cycles since the graph is then a rectangle. The graph illustrates clearly that entropy first "flows" from the hot body to the heat sink, then back from the heat sink to the hot body; at the end of a reversible cycle the entropy of the working gas returns to the initial value.

## Carnot Cycle on $T$ vs $S$ Diagrams

Let us plot the Carnot cycle in the $(T, S)$ plane (Fig. 20). The first stage is isothermal represented in the graph by a straight line parallel to the $S$-axis. The second stage is adiabatic; it is a straight line parallel to the $T$-axis. The remaining two stages are the second isothermal and second adiabatic lines; they form two other sides of the rectangle.



$A$ = area $(abcd)$
$Q_1$ = area $(abfe)$
$Q_2$ = area $(cdef)$

**Fig. 20. Carnot cycle on $T$ vs $S$ diagram.**

It will be easy to find work graphically. The amount of heat obtained from the hot body is determined by the product $T\,\Delta S$. Since the heat is withdrawn from the hot body at constant temperature, the total amount of heat withdrawn in the cycle is $T_1(S_2 - S_1)$. In the graph this value is represented by the area of the rectangle *abfe*.

Likewise we can calculate the amount of heat transferred to the heat sink. It is $T_2(S_2 - S_1)$. This value is represented on the diagram by the area *cdef*. Thus, the total amount of heat transferred from the hot body to the heat sink (and hence, the equivalent amount of work) equals the area of the hatched rectangle *abcd*, which represents the Carnot cycle. The efficiency equals the ratio of the areas of the two rectangles.

The area of the rectangle is $(T_1 - T_2) \times \times (S_2 - S_1)$.

Now it is easy to correct Carnot's arguments. If the difference $T_1 - T_2$ is the difference between levels, then the role of a falling liquid, that is, of caloric, is played by the difference $S_2 - S_1$ between the entropy values at the beginning and the end of the process and not by a substance transported by the working gas from the hot body to the heat sink.

Besides the Carnot cycle which is convenient for theoretical analysis, but is unwieldy for practical applications, there are many other cycles in which a gas is liquefied (as in steam engines), explodes (as in car engines), and so forth. A cycle may consist of isochors and adiabats (the Stirling cycle) or of isobars and adiabats (the $p$ vs $T$ cycle). Cycles can be traced both in $p$ vs $V$ and in $T$ vs $S$ coordinates. These cycles are the concern of engineering thermodynamics.

While drawing diagrams it is useful to remember that the areas in both a $pV$- and a $TS$-diagram for the same cycle are equal, the area in the $pV$-diagram being the work done, and the area in the $TS$-diagram the amount of transferred heat. We know that these quantities are equal.

## Conjugate Quantities

Let us write once again the formula for the amount of heat supplied to a system in a reversible process:

$$\Delta Q = T\,\Delta S$$

This formula resembles the formula for the amount of work done on a body:

$$\Delta A = -p\,\Delta V$$

The left-hand sides of both formulas include the quantities (heat and work, respectively) which are meaningful only so long as we operate with their increments. Both $\Delta Q$ and $\Delta A$ have clear physical meanings, but there are no quantities which could be called the heat $Q$ or the work $A$ of a body. The quantities $T$ and $p$ are similar in that the equality of temperatures and the equality of pressures are the two conditions of equilibrium, and both can be measured directly, by a thermometer and manometer, respectively.

It would be expected, therefore, that there should be something in common between the other two quantities, that is, entropy and volume. One such common property is obvious. The volume of any system equals the sum of the volumes of its parts. Likewise, the entropy of the system equals the sum of the entropies of its components. Volume and entropy are additive quantities (they are also said to be extensive in contrast to $T$ and $p$, which are intensive quantities because the $T$ and $p$ of a system equal the $T$ and $p$ of any part of the system).

The quantities $p$ and $V$ are called conjugate quantities as are the entropy $S$ and temperature $T$

## Entropy of an Ideal Gas

Though entropy cannot be measured directly, by some kind of "entropy-meter", it can be calculated theoretically. This task is the simplest for an ideal gas.

Let us take one mole of a gas at a temperature $T_0$ and let the gas occupy a volume $V_0$. Then suppose we change this state by a two-stage process to one with temperature $T$ and volume $V$. First, we expand the gas isothermally so that the volume becomes $V$ and, second, we heat the gas to temperature $T$ at constant volume.

During the first stage the gas does some work (we have calculated it already), namely, $RT_0 \ln (V/V_0)$. At this stage the gas has obtained an amount of heat equal to this work from the hot body. This means that the entropy of the gas has increased by

$$S_1 - S_0 = \frac{1}{T_0}\left(RT_0 \ln \frac{V}{V_0}\right) = R \ln \frac{V}{V_0}$$

During the second stage heating the gas by $\Delta T$ requires an amount of heat equal to $c_V\, \Delta T$. The corresponding increment in entropy is thus

$$\Delta S = c_V \frac{\Delta T}{T}$$

Now to calculate the increment in entropy when temperature changes from $T_0$ to $T$ one must add up all the $\Delta S$ contributions, taking into account that $T$ increases. This is not difficult to do if we assume that heat capacity $c_V$ is constant throughout the process.

The calculation procedure in this case is the same as for the calculation of work in an isothermal process. For a small increment in volume we had

$$\Delta A = -p\,\Delta V = -RT\frac{\Delta V}{V_0}$$

which led us to the formula (at $T$ = const)

$$A = -RT\ln\frac{V}{V_0}$$

By analogy, the increment in entropy caused by temperature changing from $T_0$ to $T$ is

$$S - S_1 = c_V \ln\frac{T}{T_0}$$

From this we directly obtain the formula of final change in entropy:

$$S - S_0 = c_V \ln\frac{T}{T_0} + R\ln\frac{V}{V_0}$$

The values of $V_0$ and $T_0$ are arbitrary; hence the formula allows us to calculate only the change in entropy but not its absolute value.

## Real, Irreversible World

Speaking about the Carnot cycles we always stressed the reversibility of all processes, but this is not the case in the real world. Take, for example, a container with a gas divided into two compartments by a thermally insulating partition. Assume that the gas in each compartment is at its own temperature and pressure. Then we remove the partition, and the temperatures and pressures start to level off. Nothing useful can be obtained from this process: the temperature difference vanishes and no apparent work is done. It is not difficult to see the reason for this "waste". The process of heat conduction, that is, the process of temperature levelling off, is irreversible: one cannot return the system to the initial state without doing some work.

This "vanishing" of the potential work is encountered everywhere. While describing an isothermal process in which heat passes from the hot body to the working gas, we observed that this process will become irreversible if there is a temperature difference, no matter how small, between the gas and the hot body. Irreversible processes will occur inside the expanding gas if the temperature of the gas is not exactly uniform throughout the volume. This is why the Carnot cycle cannot be realized, for we would have to eliminate all temperature gradients. But were this possible, heat would cease to flow from the hot body and the engine would not work.

But what happens to a gas in which an irreversible process goes on? Let us again take the container divided by a partition and calculate the change in the entropy of the gas when the temperatures level off.

The process of mixing in the gas can be described as follows: each parcel of the gas expands, increasing in volume by a factor of 2. For the sake of simplicity, we assume that each compartment of the container has half a mole of the gas in it and that the pressure is the same in both compartments. Since the temperature after mixing obviously tends to $\frac{1}{2}(T_1 + T_2)$, the change in entropy is

$$\Delta S = \frac{1}{2}\left(c_V \ln \frac{T_1+T_2}{2T_1} + R \ln 2\right) + \frac{1}{2}\left(c_V \ln \frac{T_1+T_2}{2T_2} + R \ln 2\right) = c_V \ln \frac{T_1+T_2}{2\sqrt{T_1T_2}} + R \ln 2$$

Note that this is a positive quantity because $(T_1 + T_2)^2 \geqslant 4T_1T_2$. Entropy has increased. It is only in reversible processes that the entropy of a system remains constant during which a loss of entropy in one compartment is compensated for by a gain in the other. The entropy of the hot body decreases by the value which exactly equals the increase in the entropy of the heat sink, the value of change being $\Delta Q/T$ The caloric model works well when one tries to describe the heat transfer from the hot body to the working gas. But when the working gas transfers the heat $Q_2$ to the heat sink, this heat is less than that obtained from the hot body. The entropy $\Delta Q/T$ transferred to the heat sink exactly equals the entropy withdrawn from the hot body and in a reversible process it is the entropy and not the amount of heat that is transferred unchanged from the hot body to the heat sink.

Had Carnot known this, he would have used the following line of arguments. If a cycle transfers some amount of caloric (suppose that Carnot gave this name to entropy) and this amount equals $Q_1/T_1$, then, multiplying this quantity by the temperature difference, we obtain that the work done by the engine is

$$\frac{Q_1}{T_1}(T_1-T_2)=Q_1\frac{T_1-T_2}{T_1}$$

The reader certainly recognizes in this formula the expression for the work in an ideal cycle with efficiency $\eta = (T_1 - T_2)/T_1$, this is the expression Clausius obtained many years after Carnot's death. Carnot knew that the "driving force of fire" depends only on $T_1$ and $T_2$, but he did not arrive at the mathematical relation.

Nevertheless, the caloric model cannot be saved. In irreversible processes entropy is not conserved and thus cannot be identified with caloric which, by virtue of its definition, must neither be created nor destroyed. The caloric model thus has to be dismissed.

## Price of Work

We have already said that if we tried to realize an ideal cycle, we would encounter some unsolvable problems. The main thing would be to see that the working gas's temperature is exactly equal to that of the heat sink and that the expansion and compression of the gas are very slow otherwise the temperature and pressure of the gas will not have enough time to level off. This cycle would be ideal but "good for nothing" and its power would be exactly zero, that is, any work would require an infinitely long time. In order to produce some work one has to violate the strict conditions of an ideal cycle. But as soon as these conditions are violated, heat conduction sets in, heat fluxes developing between the sections of different temperature and, as stated above, the entropy increases.

During the isothermal expansion (the first stage of the Carnot cycle) the entropy increases not by $\Delta Q_1/T_1$ but by a larger amount. Likewise, as heat is transferred to the heat sink, the entropy decreases not by $\Delta Q_2/T_2$ but by a smaller amount. As a result, once the cycle has been completed the entropy of the working gas will have increased.

This results in a very important theorem which states that a change in the entropy of a body (or system) is always greater than the ratio between the amount of heat supplied to the body (or system) and the absolute temperature of the body:

$$\Delta S \geqslant \frac{\Delta Q}{T}$$

The equality sign corresponds to a reversible (i.e. practically unfeasible) process.

A rise in entropy is the price of the real work done by a heat engine, that is, of the nonzero power of the engine.

If we want an engine to do some work, we must pay for it not only with energy consumed but also with an increase in the entropy of the system. The energy can be restored returning the work done previously. The rise in entropy cannot be brought down (without additional work), because in the reverse process it will grow still more.

It would probably be reasonable to change the sign in the definition of entropy because if something is lost it is only logical to speak about decrease. Indeed, in information theory the term used is "negentropy", that is, entropy with the sign reversed.

Entropy is not only the price of the work done, every measurement must be paid for.

A thermometer is given to a patient. At first the mercury column is very short. Then a thermal flux flowing from the patient's body to the thermometer raises the mercury column. The entropy of the thermometer increases accordingly and that of the patient decreases (although slightly). But the entropy of the patient + thermometer system increases irreversibly. It is impossible to use a thermometer in such a way that no thermal flux occurs, for this would require prior information about the patient's temperature. But this is precisely the information we lack, otherwise we would not need the thermometer.

Every measurement has its price and is paid for by entropy. In our world every gain in work and every measurement inevitably increase entropy, and this process is ubiquitous. Friction, heat conduction, diffusion, viscosity, Jole heat are some of the basic mechanisms which increase the amount of entropy.

The entropy of an isolated system increases until the system reaches the state of thermodynamic equilibrium in which all irreversible processes die out.

In the state of thermal equilibrium the entropy is at a maximum value. The reason why a gas "forgets" about the walls and collisions is that in a state of maximum entropy the gas has no currency with which to "pay" for information about the type of collisions: its entropy cannot increase any further.

## One More Formula for Entropy

We had the following formula for the entropy of one mole of an ideal gas:

$$S - S_0 = c_V \ln \frac{T}{T_0} + R \ln \frac{V}{V_0}$$

If we use the equation of state $pV = RT$ in order to eliminate $V$, we obtain

$$S - S_0 = (c_V + R) \ln \frac{T}{T_0} + R \ln \frac{p}{p_0}$$

or

$$S - S_0 = c_p \ln \frac{T}{T_0} + R \ln \frac{p}{p_0}$$

where $c_p = c_V + R$ is the heat capacity at constant pressure. One can conclude now that the levelling off of pressure at constant temperature also leads to an increase in entropy. The mechanism of pressure equalization is such that gas particles collide and transfer momentum to each other. Particles that on the average have higher velocities transfer part of their momentum to other particles, i.e. faster particles are decelerated. This is the mechanism that causes the viscosity of gases. Viscosity becomes important when there is a pressure difference in a gas (or in a liquid)*. When pressure reaches the equilibrium value, we can forget about the collisions of particles again. The equilibrium state retains no memory of collisions.

## Two Laws of Thermodynamics

Having come more than half-way through the book we can pause awhile. We already know how some rather vague ideas about heat and caloric were transformed into the concepts of entropy, temperature, and internal energy. The history of the theory of heat is like an intricate detective story since the two main quantities could neither be observed nor directly measured.

We cannot even say that the new concepts resulted from new experiments. Only Joule's experiments on the mechanical equivalent of heat may in some way be considered fundamental in this field, though Carnot and Mayer had calculated this value much earlier and needed no special experiments to do this. The elegant structure of thermodynamics is the result of a profound analysis of the unity of physical laws and of the

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*Viscosity is also a characteristic of solids, though it is more difficult to observe. Sound propagating in a solid is damped because of viscosity, and the damping in lead is stronger than in copper, and there are no acoustic vibrations in cheese.

close relationship which must exist between various natural phenomena. The success of thermodynamics proves the validity of our belief that nature obeys simple laws and that these laws can be discovered and understood. The most surprising fact about our world is its intelligibility.

The laws controlling heat phenomena turned out to be simple. Practically everything in thermodynamics is based upon two postulates which are called laws. They were formulated by Clausius and Thomson.

The first law of thermodynamics is the law of the conservation of energy. It incorporates the principle of the equivalence of heat and mechanical work (differing in this respect from the law of the conservation of energy in mechanics) and can be formulated as follows: a change in the internal energy of a system equals the sum of the heat supplied to and the work done on the system.

The second law of thermodynamics stems from the law of increasing entropy: the entropy of a closed system cannot decrease. A different formulation is possible: no process exists which results in only the cooling of one body and the doing of mechanical work. It is impossible to convert all heat into work, for the fraction of heat converted into work cannot exceed what is given by the Carnot function.

This set of postulates is supplemented with a third law which is also called the Nernst heat theorem, viz. a body cannot be cooled down to absolute zero by a finite number of steps. The Nernst heat theorem in fact follows from quantum mechanics. Nernst could not know it, but he could clearly see what this theorem meant for the theory of heat.

The two laws of thermodynamics forbid, or state as impossible, a perpetual motion machine.

The first law forbids a perpetual motion machine of the first kind, that is, a machine doing work without an expenditure of the heat or internal energy of a system. Nowadays this statement seems trivial because we are used to the law of the conservation of energy in mechanics.

The second law states that it is impossible to construct a perpetual motion machine of the second kind, i.e. the one that draws energy from a single heater, that is, it is not driven by a temperature difference but by the heat of only one body. Such a machine would be like a freezer not connected to the mains but warming the room by withdrawing heat from frozen items. There is no similar law in mechanics and it is very difficult to explain why one cannot construct a perpetual motion machine of the second kind. The law of increasing entropy is a property of our macroscopic world which, probably, cannot be reduced to other, simpler laws.

The increase in entropy also determines the direction of the flow of time. Radioactive decay, the deceleration of a parachute jumper, the energy consumption of a wound-up clock spring (or the energy of an electric battery), and finally, our own ageing are all "one-directional" processes by which we can distinguish the future from the past. It is remarkable that throughout the observable Universe time flows in one direction only. For every observer, creation precedes destruction and a cause never and nowhere occurs after the effect.

Entropy increases everywhere and always, fixing the so-called "arrow of time" and making "yesterday" different from "tomorrow".

## Refrigerator

Although cycle reversibility in a heat engine was used in numerous arguments and theories, for a long time nobody thought of the possible practical applications of a heat engine working "in reverse". For some reason the idea of a household refrigerator only emerged fairly recently. Iceboxes, i.e. refrigerators filled with ice, appeared in homes only in the middle of the last century and the electric refrigerators which now can be found in every kitchen appeared on the market only in the first decades of our century.

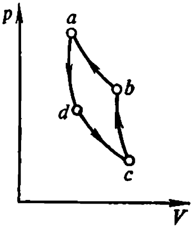

Fig. 21. A refrigerator's cycle.

Putting aside the problems of design, note only that a refrigerator operates according to the same law as a heat engine, only all the steps follow in a reverse order. Cycle $C$ is replaced with cycle $C^{-1}$ (Fig. 21 .

In the process of isothermal expansion at the stage $cd$ an amount of heat $\Delta Q_2$ passes from the heat sink to the gas which is cooled. Then the gas is adiabatically compressed to the pressure corresponding to point *b*; at this point the gas contacts the hot body (the air in the room) and transfers an amount of heat $\Delta Q_1$ to it in the process of isothermal compression ending at point *a*. This consumes some work. At the last stage the gas expands adiabatically and "returns" to point *c*. In the cooling cycle the stage *cba* is the compressor stage (in a direct cycle a cylinder with a piston does some work at this stage). In some refrigerators, which are now obsolete, the pressure was raised by heating and the heated gas was let out into a practically empty container and expanded. The expansion reduced the temperature of the gas.

A household refrigerator cools the stored food and warms up the room. When refrigerators were still a novelty around a house, an electric oven was advertized which could be turned into a refrigerator by a turn of a handle. It is unknown whether this oven was convenient and efficient, but it gave an excellent demonstration of the basic idea of a reversible thermodynamic cycle.

It is not a simple procedure to determine a quantity similar to the efficiency of a heat engine for a refrigerator. The *TS*-diagram in Fig. 22 shows that the amount of heat $\Delta Q_2$ is withdrawn from the heat sink and the hot body receives the amount of heat $\Delta Q_1$; the excess is replenished by the work done by the compressor. It may seem that this work could be made arbitrarily small provided the temperature difference between the hot body and the heat sink were also sufficiently small. But, in fact, the hot-body temperature cannot be controlled, for it is the temperature of a room. It is clear that in a very cold room the cooling of stored food will be easier than in a hot room. Depending on the conditions, the work done can arbitrarily exceed the amount of heat withdrawn. This is clearly shown in Fig. 23.

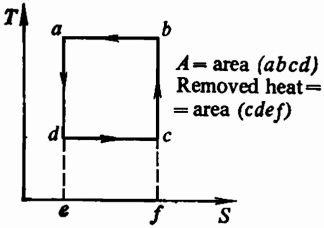

Fig. 22. Working cycle of a refrigerator (not necessarily a Carnot cycle).

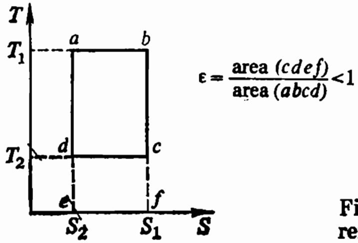

Fig. 23. Efficiency of a refrigerator.

The ratio of the work done to the amount of heat withdrawn from the heat sink, which is what characterizes the efficiency of a refrigerator, can be very small if a refrigerator reduces the temperature only slightly. However, this ratio can be arbitrarily large if the required temperature difference is large. This quantity can take on arbitrary values from zero to infinity and is also called efficiency (not to be confused with the direct-process efficiency that varies from zero to unity).

## Thomson's Heat Pump

Nowadays nobody is surprised by the fact that a refrigerator warms the room. The second law of thermodynamics states that it is impossible to construct a machine which would cool some volume without an expenditure of work.

It would be desirable to have a kitchen machine which could freeze the food and use the gained heat to cook meals without any power consumption. Alas, this is forbidden by the second law of thermodynamics.

However, if we do not demand that the refrigerator should do the impossible, but instead set it a simpler task, for example, warming the kitchen in which it is installed, the refrigerator can, or so it seems, do this almost "free of charge". Such seemingly strange device was invented by Sir William Thomson (Kelvin). He named it a heat pump.

If there is a balcony in the kitchen, the refrigerator can be put into the door opening with its door to the street and its back wall to the kitchen. Now let us open the refrigerator door and switch the refrigerator on. The refrigerator will pump the heat cooling the street and warming the room. It can transfer a lot of heat doing little work and it only requires that the temperature difference be small. Then the area of the curve representing the cycle will be small (Fig. 24) and the amount of heat transferred will be large. There is no mistake in this explanation: we simply used a high-efficiency mode of refrigerator operation, as described earlier. The heat pump is not a very useful machine, but it is an excellent illustration of the difference between the first and second laws of thermodynamics. The first law states the equivalence of heat and work, and the second indicates the difference between them: to obtain the work we have to create a heat flow. This flow necessarily entails an increase in entropy, but not necessarily a large change in the energy of a system.

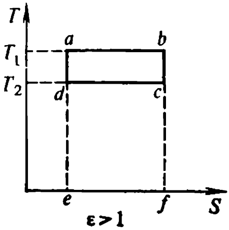

Fig. 24. Thomson's heat pump.

The apparent paradox of the heat pump is that it produces a temperature difference almost without doing work, while in the normal process of heat conduction the temperature difference vanishes without work being done. If now we construct heat engine which will use the almost gratuitous temperature difference produced by the heat pump, the amount of work done by the engine will not exceed the amount of work done to produce the temperature difference (though owing to irreversible losses the amount of work done by the engine will be even smaller). The inequality in the entropy law works honestly in one direction: it is easy to spend energy and get nothing for it, though it is impossible to obtain energy but pay nothing for it.

# Boltzmann's Formula

Thomson and Nernst virtually completed the construction of classical thermodynamics. Thermodynamics seemed to be so complete that David Gilbert's student, Constantin Carathéodory, worked out a rigorous axiomatic description of thermodynamics (by analogy with mathematics). But by the time when the "finishing touches" to thermodynamics had come to an end, a new approach to physical phenomena was developed, namely, an approach based on the kinetic theory of gases. It was necessary to combine Maxwell's results and what Thomson and Nernst had obtained. Maxwell considered the gas to be an ensemble of particles, the behavior of each particle being subject to the equations of Newtonian mechanics.

A great achievement of the kinetic theory of gases was the explanation of pressure and internal energy. The bridge between mechanics and thermodynamics looked quite safe, but it had a weak point: mechanics had no room for entropy.

Finding this room proved to be extremely difficult. When finally the problem was solved by Boltzmann in 1872, the familiar old story repeated itself: Boltzmann's work was not accepted by the majority of his colleagues. The older generation failed to see the reasons justifying the revision of what seemed to be a quite good theory of heat.

Boltzmann was able to show that entropy appears in the kinetic theory as a result of the application of probability theory to systems that previously had only been regarded from the point of view of mechanics.

The formula Boltzmann derived is very simple, viz.

$$S = k \ln w$$

It relates a thermodynamic quantity, that is, entropy, to a statistical quantity $w$ which is the probability of a state. The factor $k$ was introduced into the formula later by Planck who called it Boltzmann's constant. In physics the short formulas are charged with profound meanings. They relate the quantities which previously have been considered to be of different nature. Thus, Newton's formula $f = G\,(m_1 m_2)/R^2$ related mass to gravitation; Finstein's formula $E = mc^2$ combined two completely different concepts of classical mechanics, namely, mass and energy; Planck's formula $\hbar\omega = \varepsilon$ revealed the relation between the frequency and energy of a quantum; and Hubble's formula $v = HR$ related the recession velocities of galaxies to the distances to them. These are great formulas, and Boltzmann's formula occupies a place of honor among them. Boltzmann himself is known in the history of physics as the major founder of statistical physics.

To understand the meaning behind Boltzmann's formula, let us consider a container of volume $V_0$ filled with an ideal gas. The atoms of the gas are in chaotic motion inside the container and in the course of time each atom will have "visited" every part of the container with an equal frequency (equal probability). We would be only slightly in error if we were to assume that each atom spends half of its life in the right-hand part and the second half in the left-hand part of the container. We can also state that if the container is imagined to be divided into four equal parts, then each atom will stay in each compartment one fourth of the total time. Continuing with these arguments we can conclude that the fraction of time an atom stays in any selected volume $V$ (regardless of its shape) is equal to $V/V_0$ if $V_0$ is the volume of the container. This fact can be described as follows: the probability of finding an atom in a volume $V$ is

$$w=\frac{V}{V_0}$$

Now let us collect all time intervals when our atom (we shall designate it as atom *1*) is in volume $V$ and start monitoring another atom (atom *2*). This atom is absolutely indifferent to the behavior and location of atom *1*. Therefore, regardless of the location of atom *1*, atom *2* will also stay in volume $V$ the fraction of time $V/V_0$. This means that during a long interval $T$ atom *1* will stay in volume $V$ for a time $T_1 = (V/V_0)\ T$ During interval $T_1$ atom *2* will stay in the same volume $V$ for a time

$$T_2=\frac{V}{V_0}T_1=\left(\frac{V}{V_0}\right)^2 T$$

Hence we can conclude that the probability of finding atoms *1* and *2* together within volume $V$ is $w_2 = (V/V_0)^2$. This line of argument can be extended to other atoms as well.

Thus, the probability of finding all $N_A$ atoms (the whole mole of the gas) in volume $V$ is

$$w_{N_A}=\left(\frac{V}{V_0}\right)^{N_A}$$

This probability refers to an exotic state in which the gas in the container suddenly contracts and fills volume $V$. The Avogadro number is staggeringly large and therefore $w_{N_A}$ is very small. Thus it never happens that the gas, if left to itself, will empty even a very small fraction of the volume and that $V$ will differ from $V_0$ by any perceptible value.

If now we compare the formula for the probability to that for the entropy of an ideal gas (at $T = T_0$),

$$S - S_0 = R \ln \frac{V}{V_0}$$

or, for one molecule,

$$S - S_0 = k \ln \frac{V}{V_0}$$

we shall see that

$$S - S_0 = k \ln w$$

This is Boltzmann's formula for an ideal gas at $T =$ const. In fact, we do not actually calculate entropy, we rather calculate its increment as we pass from volume $V_0$ to volume $V$ The entropy of the initial state of the gas (temperature $T_0$ and volume $V_0$) remains an indeterminate constant. This is also true for all our later formulas.

## $S$ as a Function of Temperature

The derivation of Boltzmann's formula for a gas, in which temperature changes, is much more complicated. In what follows we do not use a very rigorous argumentation.

Let us recall what was said in sections dealing with the Maxwell distribution of velocities. Let us monitor the motion of atoms in velocity space, that is, record the changes of atoms' velocities in time. In contrast to our conventional space, that is, the coordinate space where there is an equal probability for an atom to be at any point in the space, in velocity space an atom's "coordinates" $v$ are found only in the vicinity of the mean velocity:

$$v_{\mathrm{m}} = \alpha\sqrt{kT}$$

We shall not specify whether the mean velocity is the mean square, the most probable velocity or some other velocity, nor shall we bother about the coefficient $\alpha$. As follows from the Maxwell distribution, the velocities of atoms are not exactly equal to $v_{\mathrm{m}}$, but we can say that the majority of atoms have velocities that differ from $v_{\mathrm{m}}$ by not more than $\beta\sqrt{kT}$, where $\beta$ is another constant whose exact meaning is now immaterial.

This statement can be justified if we turn to the variance, that is, the spread of $v^2$ (or energy) values about the mean value (a rigorous derivation of this is complicated). We can say that in velocity space the vast majority of molecules are in the volume all points of which are at the distance not more than approximately $\beta\sqrt{kT}$ from the point corresponding to the components of the mean velocity.

Consequently, almost all atoms in velocity space are located in a volume of about $\beta^3 (kT)^{3/2}$. If the temperature of a gas has changed to $T$, in velocity space nearly all atoms of the gas "crowded" in a smaller volume if $T < T_0$, or "expanded" to a larger volume if $T > T_0$.

To calculate the probability of such a rare event is a simple task. The course of action is the same as in the calculation of the probability that the gas "gathers" in a smaller volume of conventional space. The probability of this event is

$$w = \left(\frac{T}{T_0}\right)^{\frac{3}{2} N_A}$$

Note that the coefficients have disappeared from the formula: this was the reason why we could neglect them.

Entropy equals the logarithm of this expression times $R$. Therefore,

$$S - S_0 = c_V \ln \frac{T}{T_0} \quad (\text{at } V = V_0)$$

since $\frac{3}{2} N_A = c_V$ is the heat capacity of one mole of a gas at constant volume.

The formula we have derived coincides with that obtained in thermodynamics. But if we compare this derivation to the earlier one where the amount of heat and work were calculated without ever mentioning the probability aspect, it is surprising that such different starting points in physics should lead finally to the same formulas. Indeed, it is a characteristic feature of the present-day science that physical phenomena are considered from most diverse aspects. And to develop this ability is the very first goal of a scientist.

## Density of States

In systems governed by the quantum-mechanical laws, entropy and temperature reveal themselves in a quite different way. In a system such as, for example, the atomic nucleus, the coordinates and velocities of its constituents (nucleons) cannot be measured. Moreover, this is completely unnecessary. An atomic nucleus is characterized by allowed energy levels; these levels constitute the so-called energy spectrum of the nucleus. Each state, other than its energy, of a nucleus can be described by a number of other characteristics such as spin, parity, etc. We shall not discuss these characteristics, but they are important, for there can be many states with the same energy but differing in other characteristics.

If an atomic nucleus obtained a high energy from the outside, for example, by capturing a neutron, then after the capture the nucleus can be found in one of many "final" states with roughly the same probability. The volume of the nucleus does not change significantly, therefore the choice between final states reduces to the choice of energy. The problem then resembles the one of probability calculations in velocity space. But with a nucleus we have no information about nucleons' velocities. On the other hand, we know that a nucleus has a rich spectrum of energy levels. In every narrow energy interval (if the energy is not very low) there are many energy levels, and we can use the notion of a number of levels $\Delta n$ per unit energy interval $\Delta E$. The quantity $\Delta n/\Delta E$ is called the density of energy levels and is designated by $\rho(E)$. A nucleus capturing a neutron emits one or several gamma quanta, thereby spending a part of its own energy. The remaining energy can be different in different specific cases, and we can formulate the following hypothesis: the probability of finding an energy $E$ in an excited nucleus is proportional to the density of the levels in the neighborhood of this energy value. The greater the number of levels within an interval, the "easier" it is for the nucleus to stay in the interval. Such is roughly the gist of this hypothesis.

If we arbitrarily choose a standard, that is, a reference density for the levels, e.g. $\rho_0$, and refer the densities of the other energy levels to it, then Boltzmann's formula gives the following formula for entropy:

$$S = k \ln \frac{\rho}{\rho_0}$$

This crude formula can be used for an approximate description of systems with a sufficiently large number of degrees of freedom. For example, there is an elegant application of it in the field of nuclear reactions.

## Temperature of Atomic Nuclei

In 1937 Bohr suggested describing nuclear reactions by means of the "compound nucleus" model. The idea was to give a two-stage description of the neutron-nucleus collision. The first stage is the capture of the neutron by the nucleus. If the energy of the neutron is not high, the neutron will soon lose it. The neutron is attracted by the nucleus, and the attraction energy (or rather, a fraction of it) is "squandered" on other nucleons. As a result, a statistical distribution is established inside the nucleus. The higher the energy brought into the nucleus, the more excited the nucleus and the higher the density of the levels in the interval into which the nucleus is excited (we know that this density is a very steep function of the excitation energy).

The nucleus cannot stay long in this state. Like a heated droplet of a liquid, the nucleus must get rid of the excess energy and cool down. The excess energy will be taken away by "evaporating" particles.

This process can be described in a way similar to the evaporation of a hot droplet from a surface. The evaporating molecules are Maxwell-distributed, with the only difference here being that the distribution does not represent the stationary gas (as a whole) but the flux of the molecules escaping from the liquid. An additional factor $v_z$ in this distribution ($z$ is perpendicular to the surface) takes into account that the flux of particles is proportional to the product of their density by the relevant component velocity. To describe the process of evaporation from a nucleus we must know the temperature of the nucleus. But we only know the excitation energies and densities of the energy levels and cannot measure the temperature of the nucleus. No instrument known to thermometrists can be used to perform this task (even if only in principle). But the temperature of a nucleus can be calculated.

If we excite the nucleus, just a bit, incrementing its energy by $\Delta E$, the increment of its entropy will be

$$\Delta S = \frac{\Delta E}{T}$$

since an increase in the energy of a nucleus and an increase in the heat supplied to it are equivalent things. Substituting $\Delta S$ by its formula ($\rho_0$ can be neglected as a constant), we obtain

$$\frac{1}{T} = k \frac{\Delta \ln \rho}{\Delta E}$$

that is, the reciprocal of the temperature equals the change in the logarithm of the level density per unit change in excitation energy. The higher the excitation, the higher the density of energy levels and the higher the temperature of the nucleus.

Rewriting the last formula, we get

$$\Delta E = kT \, \Delta \ln \rho$$

and recalling what was said about the energy of the vibrational degrees of freedom, we can interpret $\Delta \ln \rho$ as a measure of the number of vibrations that contribute to the thermal energy of the nuclei at temperature $T$.

It is natural to measure the temperature of a nucleus in energy units, that is, in joules, rather than in degrees Kelvin. Doing this we at last get rid of Boltzmann's constant $k$. But the joule is a very large unit and so the temperature is measured in millions of electron volts (the same as the excitation energy of a nucleus): $1\ \text{MeV} = 1.6 \cdot 10^{-6}$ erg $= 1.6 \cdot 10^{-13}$ joule, or $1\ \text{MeV} = 10^{10}$ K.

Of course, the logical foundation for applying the concept of temperature to a nucleus is somewhat shaky. The number of the particles in a nucleus is not large and the nucleus never completely forgets its history. Nevertheless, in many cases the spectrum of the velocities of neutrons escaping from an excited nucleus is quite similar to the spectrum of the molecules that would evaporate from a hot droplet. But the distribution of particles corresponds to a very high temperature. It can be shown that the temperature of a nucleus grows according to the square root of the excitation energy and is, in energy units, between 1 and 1.5 MeV at an excitation energy of 10 MeV for nuclei with $A \approx 100$. This corresponds approximately to $10^{10}$ K, so that the neutron "vapor" over the nucleus is indeed very hot.

The velocity distribution of the particles and quanta that evaporate from a "heated" nucleus give us an experimental means for measuring the temperature of the "emitter".

Another interesting aspect of the example of nuclear temperature is that here two quantities are measured in terms of energy, namely, the excitation energy and the temperature which shows how the density of levels changes with the increase in the excitation energy. It was precisely this difference between the amount of heat and temperature which our predecessors could not grasp.

## Spins in Crystal Lattices

Imagine a crystal lattice with identical atoms fixed at its sites. Let each atom have an angular momentum, i.e. spin, and a magnetic moment associated with the spin. We have already discussed a similar system, namely, the system of electrons.

All we need to know about the atoms is that if the absolute value of the spin is $s\hbar$, then its projection on the direction of the magnetic field can assume only $2s + 1$ values, viz.

$$-s\hbar, \; -(s-1)\hbar, \qquad (s-1)\hbar, \; s\hbar$$

The magnetic moment of an atom aligns along its spin and hence its projection on the magnetic field also takes on only $2s + 1$ values.

If we denote the maximum projection of a magnetic moment by $g\mu s$, then its allowable projections will be

$$-g\mu s, \; -g\mu(s-1), \qquad ., \; g\mu(s+1), \; g\mu s$$

A three-lettered notation of magnetic moment is not accidental. Indeed, $\mu$ is a unit of measurement. If the magnetic moment originates with electrons (as in the model discussed earlier), then $\mu = \mu_0$, that is, $\mu$ is the size of the Bohr magneton, and the magnetic moment, $gs$, is measured in Bohr magnetons. If the magnetic moment originates with the nucleus, then $\mu = \mu_N$, that is, $\mu$ is the size of the nuclear magneton:

$$\mu_N = \frac{e\hbar}{2M_p c}$$

where $M_p$ is the proton mass, and the magnetic moment is measured in nuclear magnetons.

The exact values of these quantities are

$$\mu_0 = 0.578839 \cdot 10^{-8} \text{ eV/Oe}$$

and

$$\mu_N = 3.1525 \cdot 10^{-12} \text{ eV/Oe}$$

The units have been chosen in such a way that after the multiplication by the magnitude of magnetic field the energy will be in electron volts.

Finally, $g$ is the ratio of the magnetic moment to the angular momentum and this is called the gyromagnetic ratio. It can be positive or negative. For a proton $g = 2.8$, for a neutron $g = -1.9$. Some nuclei have $g < 0$ (like the Earth itself!) and others have $g > 0$.

In an external magnetic field the energy of the atom's magnetic moment is $-mg\mu_0 H$, where $m$ assumes one out of $2s + 1$ values, viz.

$$m = -s, -s + 1, \ldots, s - 1, s$$

This can be formulated in a different way. A nucleus in a magnetic field has $2s + 1$ energy levels and the spacing of the energy levels is constant and proportional to the magnitude of the magnetic field. The reader can take this statement for granted without going into the details of its derivation.

Now that the energy of each spin is known, we can calculate the energy of the whole system. Assuming for simplicity that the magnetic moments of different atoms do not interact with one another, we can calculate the energy of the system (and it is this energy and not the energy of one particle that is important for the determination of temperature) as the sum of the energies of individual constituent atoms. After this we can find the level density which is a steeply increasing function of energy. But we shall pursue a more illustrative approach and, by keeping an eye on only the energy of individual particles, we will forego a more detailed analysis.

## Spin Equilibria and Temperature

Let us start with a zero magnetic field. Then spin orientations do not affect the energy and each of the $2s + 1$ projections of the spin can occur with

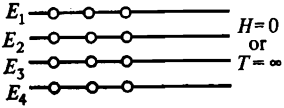

Fig. 25. Distribution of atoms in the absence of a magnetic field.

equal probability. Graphically this can be represented by drawing equal number of circles on each of the $2s + 1$ energy levels (Fig. 25). When a magnetic field is switched on, the number of atoms on each energy level remains unaltered at first although the energies of the atoms change according to the formula $\varepsilon_m = -mg\mu_0 H$.

Were the atoms completely isolated, their spins, like free magnetic needles, would not stop since stopping calls for friction in the pivots. In the case under discussion a friction-like process is represented by interatomic interactions resulting in energy exchange between atoms. This is the process through which thermal equilibrium is attained. As a result, after some time the spin distribution will fit the formula resembling that of the Maxwell distribution, i.e. the number of atoms on the $m$th energy level (energy $\varepsilon_m$) is proportional to the already familiar exponent:

$$w(m) = A \exp\left(-\frac{\varepsilon_m}{kT}\right) = A \exp\left(\frac{mg\mu_0 H}{kT}\right)$$

The constant $A$ is found because we know the total number of nuclei, $N$, say, and we must get:

$$A \sum_{m=-s}^{s} w(m) = N$$

The sum (which is a geometric progression with the common ratio $\exp(g\mu_0 H/kT)$) is easy to calcu-

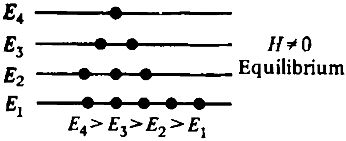

Fig. 26. Spins in a magnetic field at thermal equilibrium.

late, but just now we are not interested in details.

The spin distribution of atoms for a thermal equilibrium is illustrated in Fig. 26.

We thus see that it is possible to speak about the spin temperature of atoms. This is a quantity which determines the distribution law of spin projections in a magnetic field. If the temperature is very high ($T \rightarrow \infty$), the exponent is unity and all the $w(m)$ are equal.

The use of the energy distribution of spins in a magnetic field immediately leads to a paradox.

## Negative Temperatures

Though it is always stated (and this statement is correct) that absolute zero is the lowest temperature possible, physicists often speak about negative temperatures.

Suppose an atom has a spin of $\frac{1}{2}$, it then has two states in a magnetic field, with $m = \pm \frac{1}{2}$.

If the atom's magnetic moment is positive ($g > 0$), then the spins of the majority of the atoms align with the field, and only at $T = \infty$ do the probabilities for both directions become equal. This means that no matter how much heat is supplied to a system, it is impossible to make the higher-energy state occur more often, that is, make it more "populated", than the lower-energy state. Nevertheless, such a population inversion can be achieved by a little trick, i.e. by reversing the magnetic field rapidly. To describe the new situation we have to substitute $-H$ for $H$ in all our formulas. But this is the same as substituting $-T$ for $T$ The spin distribution after the "reversal" of the field looks as if the temperature of the spins has become negative. The higher-energy level has a larger population (Fig. 27).

What could not be done by withdrawing heat has proved to be a relatively simple task by controlling the magnetic field. The system has only a few levels, and it is possible to make them "swap places"

What will happen in the system after the reversal? It is clear that the system of spins will return to thermal equilibrium. Spins will reverse owing to the electromagnetic interactions of atoms. The energy excess will dissipate to other parts of the system, and the spin distribution will tend to an equilibrium at $T$. This process closely resembles heat transfer in which the excess energy is transferred to the parts at lower temperatures. Evidently, the excess appeared when the system of spins acquired some additional energy by the field reversal.

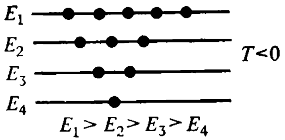

Fig. 27. Distribution for a "negative" temperature.

This result can be described in a more formal way. Let us write the ratio of "populations" for the two levels:

$$\alpha = \frac{w(\varepsilon_1)}{w(\varepsilon_2)} = \exp\left(-\frac{\Delta}{kT}\right)$$

where $\Delta \quad \varepsilon_1 - \varepsilon_2$ is the energy difference between the levels. The formula shows that in a "normal" situation, when $T$ changes from 0 to $\infty$,

$\alpha$ changes from 0 to 1, and the interval of $\alpha$ from 1 to $\infty$ (the upper level is more populated) can be compared with the values of $T$ from $-\infty$ to 0. The population is described by a discontinuous function of $T$; an equal population of two levels has two values of temperature corresponding to it: $T = \pm\infty$, since $\alpha(\pm\infty) = 1$.

The relative population of the upper level ($\alpha$) is thus described in terms of temperature in a paradoxical way. The population grows when temperature increases from zero to infinity. However, $T = \infty$ does not correspond to the largest value of $\alpha$. The population can grow further (from 1 to $\infty$) if temperature increases from $-\infty$ to 0. In this respect we can say that negative temperatures lie "higher" than $T = \infty$. It would be more convenient to describe the behavior of $\alpha$ by using a quantity reciprocal to temperature, namely $\beta = 1/T$ It is clear that when $\alpha$ changes from 0 to $\infty$, $\beta$ monotonically decreases from $\infty$ to $-\infty$ without discontinuity. "Reciprocal temperature" $1/T$ is in many cases a preferable characteristic.

Population inversion is used in lasers.

When there are only two energy levels, temperature is readily given by the logarithm of the population ratio. However, if there are many energy levels, the situation is more complicated. And the "wrong" population of levels cannot be described by a single parameter, that is, temperature.

When the energy of all the levels, $\varepsilon_m$, can be switched to $-\varepsilon_m$, the concept of negative temperatures has a clear-cut meaning. And this is the case of spins in a magnetic field. We know that if the spin of an atom is $s$, the system has $2s + 1$

states and its energy values constitute an arithmetic progression. The levels are equally spaced and the replacement of $H$ with $-H$ changes only the order of the levels without changing their spacing; as a result the pattern of the level is not distorted. This was the reason why we used the magnetic moment as the study case.

But if the pattern of energy levels is not that simple and the levels are not uniformly spaced, we cannot organize the population inversion in a simple manner and, strictly speaking, the notion of negative temperature has no meaning. However, here we can speak about temperature being different in various parts of the energy spectrum and choose the parts in such a manner that the levels inside them can be assumed to be equidistant. Equilibrium is again reached through changes in level population tending to the "correct" equilibrium distribution. As before, the second law of thermodynamics determines the direction of the thermal fluxes and thus shows which parts of the spectrum lose and which gain energy.

Unequal spacing is characteristic of atoms with complex magnetic-moment systems produced by the motion of many electrons and their spins. The concept of negative temperatures has become important in optics, especially in laser physics.

In all our considerations it was indispensable that the energy spectrum of the system was bounded. Only then has a system a ground level and a highest energy level, and thus can be "inverted", that is, we can replace $T$ with $-T$ and obtain the picture described formally by a negative temperature.

The concept of negative temperatures is inapplicable to translational motion whose energy can vary from 0 to $\infty$, so it is impossible to produce a distribution which would correspond to negative temperatures.

## Maximum Temperature

Is it meaningful to ask which temperature is the highest possible? We know the lowest temperature possible (absolute zero), although the subject proved fairly complicated. The behavior of physical systems in the vicinity of absolute zero is understood only in terms of quantum mechanics operating with energy levels. But it appears at first glance that a maximum temperature is nonsense. Evidently, the more heat is supplied to a system and the longer the system is heated, the higher its temperature climbs. Indeed, temperature is different in different systems, and it is difficult to imagine a body with an infinitely large heat capacity such that no amount of heat would be sufficient to heat the body up a single degree. Our everyday experience makes us believe such bodies are impossible.

But one has to learn that quantum mechanics often produces paradoxes that seem ridiculous from the unsophisticated, conventional standpoint. A hero who can dive into boiling water and then jump out intact occurs only in fairy tales. In the real world we learnt that the temperature of a body subjected to heating increases. But even here quantum mechanics gives an unexpected answer. It does prove possible to think up a system that does not warm up, whatever the amount of heat supplied to it. True, we can no more than imagine it, for nature does not seem to have such a system. Nevertheless, it would not contradict physics.

We saw that the temperatures of atomic nuclei are determined by the arrangement of their energy levels, namely, by the dependence of the level density, $\rho$, on the energy, $E$. The temperature of nuclei depends on the supplied heat referred to as the excitation energy and is given by the formula

$$\frac{1}{kT} \propto \frac{\Delta \ln \rho}{\Delta E}$$

This formula immediately shows that if the level density increases with energy in such a manner that $\ln \rho$ is proportional to energy, that is, $\ln \rho = AE$ ($A$ is a constant), an increment $\Delta E$ in energy increases the logarithm of the level density by $A\ \Delta E$, and temperature $T$ remains constant and equal to $1/kA$. Therefore, if we want to have a system with the maximum temperature, that is, a system in which at all times $T = T_{\max}$, this system must have the level of density at high excitation energy described by the formula

$$\rho \propto \exp(AE)$$

or $\rho \propto Q^{AE}$; with an arbitrary base $a$, $\rho \propto a^{AE}$ and the maximum temperature $T_{\max}$ equals $(1/k)\ (A \ln a)^{-1}$.

It will be useful to analyze in more detail what could bring about such a strange result.

Let us take an elementary system: a ball fixed to a spring. This system is an oscillator vibrating at a frequency $\omega$ (in this example we need an unbounded energy spectrum and thus have to reject a system of spins).

It can be proved in quantum mechanics (at first it was a daring hypothesis made by Planck) that an oscillator's energy can only be an integer multiple of the "energy quantum" $\hbar\omega$, that is, $E = n\hbar\omega$ ($n = 0, 1, 2, \ldots$). Hence, the arrangement of the levels is such that the energy levels are equidistant and all spaced by $\hbar\omega$. Hence, the level density (obviously, an interval $\Delta E$ contains $\Delta E/\hbar\omega$ levels) is independent of the energy, and, according to our formula, $\Delta \ln \rho/\Delta E$ is zero, that is, the "temperature" in this system is always infinite ($1/kT = 0$). This result is simply meaningless because we cannot speak of the temperature of a single vibrating sphere. Let us take many such oscillators, with vibration frequencies slightly differing from one another. The energy of all such oscillators is given by the sum

$$E = \hbar\,(n_1\omega_1 + n_2\omega_2 + \ldots)$$

where $n_1, n_2, \ldots$ are integers, and $\omega_1, \omega_2,$ are somewhat different frequencies.

Clearly, by specially varying the integers $n_1$, $n_2, \ldots$, we can obtain a system of energy values in which the spacing of neighbor values of $E$ will be the smaller, the larger is $E$. The density of levels will increase with increasing $E$, and the rate of increase will be the steeper, the greater the number of oscillators (spheres).

The degrees of freedom in quantum systems can be "frozen out", and the number of degrees of freedom may grow with increasing temperature. In our model of oscillating spheres we can assume that the number of the oscillators participating in the thermal motion increases very steeply as the energy of the system increases. Then we can imagine that beginning with some temperature all the heat added to the system goes into "de-freezing" additional oscillators, thus introducing new degrees of freedom, so that the energy per oscillator remains constant. This will mean that the temperature of the system of oscillators does not change. The temperature is related to the energy per degree of freedom, and the number of degrees of freedom multiplied by this mean energy gives the total energy of the system.

We will soon show that it is the freezing of the degrees of freedom that saved physics from the ultraviolet catastrophe and led to Planck's formula for radiation.

The system discussed in this section is rather artificial but it gives a clear illustration of the relationship between energy and temperature and shows how these quantities describe different properties of the system. It was not an easy task for physicists to digest these notions. Indeed, paradoxes are encountered even nowadays.

## Masses of Elementary Particles

In our story about temperature we pass from one field of physics into another. Now that we have discussed maximum temperature, we again turn to a new field, that of elementary-particle physics. There we shall find real manifestations of the paradoxical properties we described above. Our subject concerns some theories which strive to explain (or rather, to describe) the masses of elementary particles. The existence of a large number of elementary particles with very different masses has been a long standing puzzle for physicists. It is natural to hypothesize that the masses of mesons (particles with zero spin) can be calculated as the values of energy of systems composed of a quark and an antiquark, and the masses of baryons (spin-$\frac{1}{2}$ particles, including protons and neutrons) as systems composed of three quarks. At any rate, this approach was used to find the energy levels in atoms and the masses of nuclei (although only very crude approximations of them since the theory of nuclear forces is still in pretty bad shape).

Unfortunately, very little is known at present about the interactions between quarks, and still less about the gluons which are the particles (quanta of field) mediating interactions between quarks. Consequently, at the present physicists operate with only much simplified theories, or models of the quark-gluon interactions, and try to discern some general features of the complete future theory.

These models have revealed a quite general property, namely, the mass spectrum of particles is exponential. This means that the number of states in these models, that is, the energy levels that we interpret as elementary particles, is very high and grows steeply as energy increases (i.e. as mass increases).

The number of elementary particles in these models is such that the number in the interval between $m$ and $m + \Delta m$ is proportional to exp $(m/m_0)$, where $m_0$ is a constant approximately equal to 200 MeV.

We leave aside the question as to whether such a description is meaningful; it is definitely very schematic, but for now it is merely an example of a system with a maximum temperature. Recalling the formula used in the preceding section we notice that the limiting temperature $T_0$ equals $m_0$. Since one electron volt corresponds to $10^4$ K (this is readily verified if you remember that Boltzmann's constant, $k = 1.4 \cdot 10^{-16}$ erg/deg, corresponds to the energy in ergs equivalent to 1 K), then

$$T_0 = 200 \cdot 10^6 \cdot 10^4 = 2 \cdot 10^{12}\ \mathrm{K}$$

This is by far the highest temperature we have ever met.

This time we are dealing with a concrete model and so can ask what physical process takes place at $10^{12}$ K, i.e. when the mass of an elementary particle reaches 200 MeV (this occurs in the model; what takes place in reality is an altogether different thing). At this energy the particle starts to "melt", and a system of baryons, a nucleus, for instance, transforms into a drop consisting of quarks and gluons; this boiling consumes all the energy fed into the system, and for this reason its temperature ceases to increase. This is the outcome of conclusions that at first glance looked implausible.

## Unexpected Paradox

After this acquaintance with an instructive system whose temperature cannot be increased, let us pose another question. What should happen if the level density of a system rises even more steeply? There seem to be no factors in physics to limit the rate of growth of this density.

Clearly, we must be prepared for something unexpected to happen with such a system; this justifies spending some more time on this topic.

Assume that the density of levels increases exponentially but with the exponent $BE^2$ instead of $AE$. What should happen in a system if the level density is the following function of energy:

$$\rho(E) \propto \exp(BE^2)$$

By differentiating we obtain

$$\frac{\Delta \ln \rho(E)}{\Delta E} = 2BE$$

(actually, $\ln \rho(E + \Delta E) - \ln \rho(E) \cong 2E\,\Delta E$) and so

$$T = \frac{1}{2BE}$$

We see that this imaginary system possesses truly paradoxical properties. When the energy of the system increases, its temperature decreases. Of course, even this can be explained away in the sense already discussed, by referring to the very steep rate of growth of the number of degrees of freedom, but the paradox remains all the same. If this system gives away its energy, if it emits light, for instance, its temperature increases. The more this "oven" heats up the ambient medium, the more it is heated up itself. We cannot deny that this is a paradox. The way out of the quandary may lie in the possible instability of this system which, having heated up to a sufficient degree, will explode (or at least burn up). The very notion of temperature becomes somewhat uncertain in such systems, as it is uncertain in a camp-fire.

In this last example everything is quite clear: the fire temperature changes unpredictably from point to point and from time to time. Nevertheless, our system possesses most unusual properties. Furthermore, a system with such anomalous temperature behavior may indeed exist in our Universe. I mean the awesome by-product of gravitational fields: black holes. We will discuss black holes later in the book.

## Low Temperatures

The interest in low temperatures and their production has existed independently of their possible applications. Physicists had been interested for a long time in finding out whether it was possible to liquefy gases, such as air, oxygen, and hydrogen. The story begins at the end of the 18th century.

In 1783 Antoine Laurent Lavoisier wrote: "...provided we could submerge the Earth into a very cold region, for example, into the atmosphere of Jupiter or Saturn, then all our rivers and oceans would turn into mountains. The air (or, at least, some of its components) would cease to be invisible and would turn into liquid. A transformation of this kind would lead to a possibility of obtaining new kind of liquids about which we are completely in the dark."

Lavoisier could not see other ways to liquefy the air except by transporting it to a cold planet.

It was a routine procedure to produce heat, but even imagination failed to "create" cold. (Remember the "Snow Queen" by H. C. Andersen. Even she could not produce cold and had to live in the North.)

Lavoisier himself had made no attempt to liquefy any known gas, but shortly afterwards Gaspard Monge and Jean-François Clouet succeeded in liquefying sulphur dioxide by cooling it with a mixture of ice and salt.

In 1790 van Marum and Paets van Troostwyk, compressing ammonia to see whether it obeyed Boyle's law, obtained some drops of liquid. In 1799 Guyton de Morveau liquefied ammonia by cooling the gas to the temperature of a mixture of ice and calcium chloride. In 1805 Northmore obtained chlorine under the pressure of 15 atmospheres.

In 1823 Davy and his assistant Michael Faraday read their report on the liquefaction of chlorine hydrate to the Royal Society. Carbon dioxide was obtained in the liquid phase ten years later by Thilorier.

At the same time (1822) Charles Cagniard de la Tour made the very important discovery of critical points and described the continuous transition between the gas and liquid phases. But all this work stood isolated for almost half a century.

In 1877 the mining engineer Louis Paul Cailletet found some drops of liquid acetylene in a laboratory container in which a leakage had suddenly occurred and abrupt decreases in pressure caused fog condensation. Nearly at the same time Raoul Pierre Pictet from Geneva reported a step-by-step (cascade) liquefaction of various gases by evaporating them in a vacuum; the process resulted in the isolation of liquid oxygen at —140 °C and 320 atmospheres of pressure. The temperature in Cailletet's experiments was estimated to be —200 °C. Engineers started to design refrigerators and in 1879 the first refrigerator ship loaded with meat was sent from Australia to England. Apparently, the first patent for a refrigerator, dated 1887, was granted to Sir William Siemens. All these installations produced little cold. Air was liquefied by Georges Claude in 1902. All of these methods of liquefaction were based upon the cooling of a gas as it expands and does work (in a piston or turbine engine), or as it expands into a vacuum when the work is done against the forces of molecular attraction inside the gas.

In this story we must also mention Sir James Dewar who liquefied hydrogen in 1898 and so lowered temperature to about 129 K. Finally, in 1908, liquid helium was obtained by Heike Kamerlingh Onnes in Holland and the temperature he obtained was a mere one degree above absolute zero.

In 1939 Petr Leonidovich Kapitsa proved high efficiency of liquefying machines in which a gas does work on a turbine. Since then turboexpanders have come into wide use. Kapitsa also designed an effective machine to liquefy helium.

## Magnetic Cooling

The diagram of atomic energy levels in crystals will help us to understand the principle of an interesting cooling technique that could be devised only after quantum mechanics had been mastered.

At low temperatures almost all motion stops and both the translational and rotational motion die out. However, the spins of atoms continue to behave as the atoms of an ideal gas even at temperatures below 1 K, they exchange energy (although the exchange is weak) and they are almost free to change their position in space (their projection on the direction of a magnetic field). In elements such as the rare earths, electrons fill the inner shells of atoms, and their spins are almost insensitive to other electrons. Hence, magnetic moments are also nearly free.

This property of electrons underlies a method, magnetic cooling, of producing ultralow temperatures.

If we put a crystal including the atoms of a rare earth into a magnetic field and arrange that the crystal remains at the same temperature (i.e. the field is switched on isothermally), after some short interval all the magnetic moments (if they are positive, i.e. if $g > 0$), as we have already explained, will point in the direction of the field or, so to speak, point southward. If the field is now rapidly switched off, a very unusual situation will arise. There is no magnetic field, but all the spins are pointing in the same direction and not randomly as would be the case for thermal equilibrium. Actually, we assumed that the only process in the system is the motion of the spins, and the motion of the atoms is negligibly small. Now we have to refine the picture. In reality the atoms in a crystal lattice vibrate because the lattice is at a nonzero temperature $T$. The intensity of the vibrations is determined by the value of $T$. The motion of the atoms is transferred to the spins because the motion of charges generates a weak variable magnetic field. The spins are thus not in complete isolation but in a thermostat at a temperature $T$.

When an external magnetic field aligns all the spins into a single direction, the ordering this produces cannot be sustained without a field. The orientations of the spins must change (as a result of interaction with vibrating atoms) and tend to become random so that any of the spin projections would have equal probability. This process must be accompanied by an energy exchange between the spins and the atomic vibrations.

However, it is not easy to conclude at first glance the direction of energy transfer, whether atomic vibrations will be enhanced or attenuated.

In order to answer this question we have to resort to the concept of entropy. The entropy of spins must increase and hence a heat flux from the lattice (the atomic vibrations), which is at thermal equilibrium, to the spins must set in so that the spins will return to the chaotic state and the atomic vibrations will slow down slightly.

This means that the crystal cools down, this being what the theory predicts. Figure 28 shows schematically how temperature and entropy change in such a system. The upper curve describes the entropy of a crystal as a function of temperature for a zero external field and the lower curve gives the same function with the external field switched on. When the field is rapidly switched off, without changing entropy (this is what we call the adiabatic demagnetization), the temperature drops because points with the same $S$ lie on different curves for different $T$ Experiments

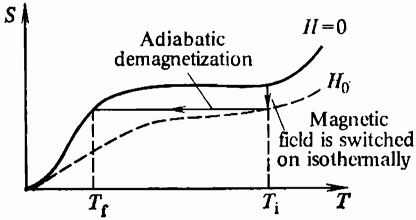

Fig. 28. Adiabatic demagnetization. Entropy as a function of temperature in a zero magnetic field ($H = 0$) and in a nonzero magnetic field ($H = H_0$).

confirmed these predictions. Could it be possible to invent such a cooling technique without knowing the subtleties of the theory?

The magnetic cooling technique was suggested in 1926 by William Francis Giauque in the USA and independently (or even a few weeks before) by Peter Debye in Germany. This method has lowered the temperatures achievable to approximately 0.003 K. Lower temperatures cannot be obtained this way because spins stop moving freely and the ordering produced in them by spin-spin coupling (an effect like the one that occurs between compass needles over short distances) is not disrupted by the weak thermal motion of atoms.

It is possible to go even lower down the temperature scale if very high magnetic fields (using tens of thousands of an oersted) are used. Such fields orient the magnetic moments of the nuclei, and all the operations are performed with the nuclei of the crystal.

In 1956 F. E. Simon used this technique to record a temperature of 0.000016 K. Unfortunately this record is not quite realistic. Atomic nuclei do interact with electrons but only very weakly (in spectroscopy this interaction is called hyperfine) and can withdraw practically no entropy from the lattice. The nuclei slowly do in fact heat up, but the lattice temperature does not decrease because the lattice manages to replenish the lost heat from the ambient despite the ingenious efforts of experimenters. The road through to the millikelvin range (thousandths of one degree) seemed blocked. How could a piece of matter, rather than an illusory system of spins, be cooled down to 0.001 K or below?

Even this has proved to be possible.

When a salt is dissolved in a solvent, the temperature of the solution drops and this simple and well-known effect has helped physicists. It was found that if helium—atomic weight 3 ($He^3$)—is dissolved in ordinary liquid helium, the temperature of the solution decreases. This process can produce temperatures down to 0.001 K.

But an even cleverer method was invented by Isaac Pomeranchuk. His invention also involves $He^3$.

In order to clarify how his method works we have plotted the entropy curves of two phases of $He^3$, one solid and one liquid, in the vicinity of absolute zero (Fig. 29). According to quantum mechanics, all systems are at their lowest state at absolute zero and the entropy of this state is zero whilst the energy is at a minimum. To be precise, the entropy is constant and the same for both phases. A comparison of the absolute values of entropy for different substances that do not transform into each other is meaningless. It is very important that at $T = 0$ both phases have the same entropy and that the transition from one phase into another does not change either the entropy or the energy. This property was postulated by Nernst and represents one of the formulations of the third law of thermodynamics.

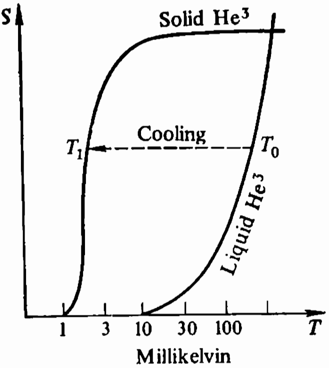

Fig. 29. Entropies of He³ in the liquid and solid phases.

What is important for Pomeranchuk's technique is that the curves are arranged in such a manner that the entropy of the solid phase is greater than that of the liquid phase. Were the arrangement different, the method would not exist.

The gist of the method is clear from Fig. 29. The plot shows that if the helium is cooled by the adiabatic compression of the liquid, converting it into a solid, then the temperature of $He^3$ will be reduced. A temperature of about 1 mK has now been achieved with this technique. At 2 mK liquid $He^3$ becomes superfluid like $He^4$ and an extremely complex and interesting world of physical phenomena is now being unveiled in this field. Unfortunately, a description of these phenomena goes far beyond the scope of this short book.

Pomeranchuk's technique even at first glance resembles cooling by adiabatic demagnetization. In fact the analogy is even more profound. The cause of the effect is due to the fact that the nuclei of $He^3$ have nonzero spins (ordinary $He^4$ has spin-0 nuclei). At very low temperatures the spins of neighboring atoms in liquid $He^3$ tend to align themselves parallel to each other, like magnetic needles. Of course, this ordering is not a long-range effect but nevertheless there is some spin ordering in liquid helium, while in solid the spins are "scattered" randomly down to a temperature of around 0.003 K. Consequently, a transition from the liquid to the solid phase resembles the adiabatic switching-off of magnetic field (when the spin directions become randomized), and a reversed transition resembles magnetization. The entropy of the solid phase is greater (at the same temperature) than that of the liquid because of spins. Actually the pattern of spin alignment in solid $He^3$ is more complex, but the above crude description is sufficient to explain the effect.

Low-temperature physics is now entering a new era and many surprises are in store for us in the millikelvin range. But is there any limit to the technical achievement beyond this range? In fact, physicists have gone even lower down the temperature scale, the most recent record being set by the Finnish physicist O.V. Lounasmaa. His record mark is 50 nanokelvins, or $50 \cdot 10^{-9}$ K.

What sort of physics will open up to our eyes in the nanokelvin range where, according to classical mechanics, all types of motion must be completely absent? Nature's secrets are much more interesting than that.

The realm of the deep, extremely deep cold is a kingdom in which effects of quantum mechanics are all-powerful. This is the land of the Snow Queen, of quantum laws that are grotesque and bizarre from our "warm-blooded" viewpoint.

## Problem for Fun

We have related quite a lot above about temperature and thermal processes. The reader should realize how difficult it was to discover entropy in heat-transfer processes and how the appearance of entropy in physics has transformed the whole science. It will probably be useful to demonstrate with a simple example how temperature and entropy work together.

We shall illustrate the notion of entropy with an example from hydrodynamics.

Imagine two reservoirs with unequal levels of water. Water can flow from one reservoir to another. Let us install a turbine in the conduit connecting the reservoirs and use the turbine to "accumulate" energy, like a battery, by lifting a weight up some way. We also install a pump which, when necessary, pumps water back. The result is a primitive model of a hydroelectric power station. If friction losses are absent (which is certainly unrealistic), you can easily see that water will flow from one reservoir to another until the levels become equal. The potential energy of water is converted into the potential energy of the weight. By letting the weight go down, we can pump all the drained water back with our pump. Obviously, we cannot return all of it because some losses are unavoidable, but we can neglect this and regard our setup to be reversible.

Were there no turbine, the levels would ultimately become equal with energy converted to heat, so that none of it would be available for pumping the water back. By accumulating the energy we can use it for different purposes. Thus, we can pump water up from a third reservoir located still lower into the uppermost reservoir. To be brief, we can do anything allowed by the law of the conservation of energy.

Now let us design a heat engine as similar to that described above as possible.

Let us take three cubes of identical size and made of the same material. Two of the cubes are at 300 K and the third at 100 K. In addition, we have a heat engine which can work with an arbitrary temperature difference. What is the maximum temperature to which one of the cubes can be heated?

First we take the 100-K cubes and a 300-K cube and press them together. The temperatures of the cubes will level off. Assuming for simplicity that the specific heat of the material of the cubes is unity and does not depend on temperature, we immediately find that the final temperature will be 200 K but part of the energy will be irreversibly lost. At least this part of the energy can be converted into work by connecting our heat engine.

In order to find what work can be retrieved, we have to use the second law of thermodynamics. Work will be maximized if the process is reversible, i.e. if the entropy of the whole system is not increased and hence

$$\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}$$

We remind the reader that $Q_1$ is the heat withdrawn from the hot body at a temperature $T_1$, and $Q_2$ is the heat transferred to the cold body at a temperature $T_2$. When the heat $Q_1$ was removed from the hot body, its temperature was reduced by

$$\Delta T_1 = -\frac{Q_1}{c} = -Q_1$$

because the specific heat $c = 1$. Likewise, the amount of heat $Q_2$ supplied to the cold body increased its temperature by

$$\Delta T_2 \quad Q_2$$

Now we recall the condition of reversibility given earlier. Substituting the expressions for $Q_1$ and $Q_2$ into it, we rewrite this condition in the form

$$T_1 \Delta T_2 + T_2 \Delta T_1 = 0$$

This condition can also be written in a different form:

$$(T_1 + \Delta T_1)\,(T_2 + \Delta T_2) = T_1 T_2$$

if we neglect a small term $\Delta T_1 \cdot \Delta T_2$. This equality signifies that when a reversible process changes the temperatures $T_1$ and $T_2$ by $\Delta T_1$ and $\Delta T_2$ (obviously, the signs of $\Delta T_1$ and $\Delta T_2$ are opposite, viz. when $T_1$ increases, $T_2$ decreases), the area of the $T_1 \cdot T_2$ rectangle remains unchanged, viz.

$$T_1 T_2 = \text{const}$$

This is the relation that must be satisfied by the temperatures of two cubes at the beginning and end of the process, provided the process is reversible.

Now we have everything necessary for the calculations. We start by constructing a heat engine out of the cubes with $T = 300$ K and 100 K. When the temperatures are equalized in a reversible process, the final temperature $T$ will be found from the relation

$$T_1 T_2 = T^2$$

Therefore, $T = (300 \cdot 100)^{1/2} \approx 173$ K.

The simplest suggestion is to convert the work obtained at the first stage into heat and transfer this heat to the third cube. Its temperature will thereby rise to 354 K.

This follows from the law of the conservation of energy, i.e. the first law of thermodynamics. The energy of our cubes is numerically equal to their temperature so that the work stored at the first stage is

$$A = 300 + 100 - 2 \cdot 173 = 54$$

However, this solution is not correct! The correct sequence is to use the stored work in a refrigerator cycle, cooling the system of two cubes at $T = 173$ K and heating the cube at $T = 300$ K.

The new stage is described not by the condition $T_1T_2 = \text{const}$ but by another one:

$$T_3T^2 = \text{const}$$

Squared $T$ appears because the cooling of a system of cubes is described by the condition $Q = -2\Delta T$, i.e.

$$\Delta S = -\frac{2\Delta T}{T}$$

and by the Carnot equation which now turns into

$$2T\,\Delta T_3 + T_3\,\Delta T = 0$$

Using almost the same arguments as before, we arrive at the condition we had before, i.e. $T_3T^2 = \text{const}$. By denoting the final temperatures by $x$ and $y$ we find that

$$T^2T_3 = x^2y$$

One equation for two temperatures is insufficient. The second equation follows from the first law:

$$A + 2T + T_3 = 2x + y$$

Substitution of the values of $A$, $T$, and $T_3$ yields the system

$$x^2y \quad 300^2\cdot 100$$

$$x + 2y = 700$$

The solution can be found after several trials and the ultimate result is

$$x = 150, \; y = 400$$

The temperature of the hot cube can thus be increased to 400 K, the other two cubes being cooled to 150 K.

## A Different Solution

The arguments in the preceding section can be minimized and made almost automatic if we introduce entropy. For a cube whose heat capacity is constant, the entropy is

$$S = k \ln T + C$$

where the constant $C$ is temperature-independent. This expression can be derived for an ideal gas and the derivation used only one property of the gas, i.e. the independence of its heat capacity on temperature. Hence, it holds in the present case as well.

The condition of reversibility indicates that the entropy of a system consisting of three cubes remains constant. Maximum heating of one cube is obviously achieved when the temperatures of the other two become equal (otherwise more work could be obtained by using them). Recalling that the entropies of the cubes add up, we find that

$$\ln x + \ln x + \ln y = \ln 300 + \ln 300 + \ln 100$$

or

$$x^2 y = 300^2 \cdot 100$$

i.e. the first equation that took much longer to derive in the preceding section. Naturally, the second equation remains the same.

If we try again to compare the three-cube problem with that about the three reservoirs, we notice that the part of potential energy is played by the logarithm of temperature, i.e. by entropy, and that the law of the conservation of energy is replaced with two laws of thermodynamics, the first determining the sum of temperatures, and the second the sum of their logarithms. The condition that the cubes have equal masses corresponds to the condition that the reservoirs have equal areas in the second problem. The main feature of the three-cube problem is that the second law of thermodynamics forbids lowering the temperature of a cold cube by any means. In the three-reservoir problem the work obtained from one turbine can be used to lower the level of water in the third, lowest reservoir.

A comparison of the two problems is very useful.

In addition, we can also recall what we said about low temperatures. The formula $S = k \ln T$ cannot be correct if temperature is low. Entropy cannot tend to $-\infty$ close to $T = 0$ but must tend to zero because at $T = 0$ any system is completely ordered and its entropy must vanish. One must be careful, therefore, about what temperature is discussed. For the temperatures chosen for the above problem everything is correct.

## Blackbody Radiation

When the caloric theory was still popular, a great deal of discussion centered on the fate of the caloric if heat was lost by radiation.

In the Carnot cycle heat was withdrawn from the hot body by the expanding gas. In the gas the heat was spent on increasing the kinetic energy of molecule so that the physical process of heat transfer, i.e. how and where the heat was transferred to, was simple and clear (of course, only after the kinetic theory of gases had won the battle). But heat is not only transferred from one body to another when they are in contact. The Sun transfers heat to the Earth via the vacuum of space and even Archimedes knew that thermal rays could be focused by means of large mirrors. Many physicists experimented on the focusing of thermal rays in the 18th century*. Finally they concluded that light and heat are the same type of phenomena and thus heat, like light, is a manifestation of vibrations in ether. The misconception took a long time to die.

Sometimes nature tricked physicists into comical situations. When everyone was sure that light propagation required ether, the ether proved to be superfluous. When physicists were certain that heat was a caloric substance which existed independently and required no carrier, it was proved that no caloric exists and that heat is transported by electromagnetic waves.

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*The term "radiant heat" first appeared in 1778 in a book called *On Light and Fire* by Carl Wilhelm Scheele. Scheele had noticed that in addition to the heat that rises above the fire with the air, there is another sort of heat that is felt when facing the flame. But heat could not be transmitted through glass, while light could, and this puzzled scientists for a long time: "Undoubtedly, light and heat are different things" was their conclusion.

But if light transfers heat, then in principle it can be the working substance in a heat engine. Then light must carry energy (this is easily comprehensible), entropy, and temperature. Moreover, thermal equilibrium must also be meaningful for light.

If Newton were right and light consisted of particles, its description as an ideal gas would stand a chance of success. But although light consists of photons, we cannot say how many photons there are in a given volume because the photons are absorbed and reradiated by the walls of their container and their number cannot be determined. We shall see that even the mean number of photons is a function of temperature.

A heated body emits light, thus we get: infrared radiation at low temperatures*, visible light at high temperatures, and galaxies in space emit in the X-ray and even $\gamma$-ray bands. The radiation emitted by any source is described by the properties of its spectrum, i.e. by indicating the energy it emits in each segment of its spectrum. A distribution function for radiation has a similar meaning to a velocity distribution function of atoms. If we start with a histogram, i.e. a diagram showing how much energy is contained within a $\Delta\nu$-wide interval of the spectrum around $\nu$, this histogram can later be

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*It should be recalled that the radiation emitted by a heated body contains, in the general case, all frequencies, but energy is mostly concentrated in a relatively narrow band of the spectrum. The problem that occupied physicists at the end of the 19th century was to find where this spectrum band (the maximum of the spectrum) lies and what its shape is.

replaced with a continuous function and we can speak of the energy density of the radiation.

The notion of the temperature of radiation and of the distribution function for the spectrum of the radiation emitted by a heated body was the first success of the new physics. A great deal of work went into making the idea of thermal equilibrium useful for describing radiation. First it was necessary to consider a closed volume in which electromagnetic waves exist. Waves can be emitted and absorbed by the walls of the container, kept at a constant and known temperature $T$.

Now we usually call such a container a resonator, or cavity. As a rule, the electromagnetic field within the resonator has a very narrow spectrum, almost monochromatic, but the resonator can be "detuned" so that it can contain waves with very differing frequencies.

The radiant heat, using the 19th century term, continuously drains from the walls into the resonator; however, the walls cannot let off their energy indefinitely and a thermodynamic equilibrium, determined by a single quantity $T$, is finally reached. The energy emitted by the walls into the thermal equilibrium must be exactly compensated for by the energy absorbed by the walls. This compensation must be true for every interval of radiation frequency. It is only natural to assume that equilibrium radiation has the same temperature as the walls.

Very general arguments enable us to state that the electromagnetic field inside the resonator is, as a system, indistinguishable from an ideal gas, in the sense that the field exchanges energy with the walls (radiation is absorbed and emitted) and that this process leads to the thermal (thermodynamic) equilibrium.

When this problem was formulated, the solution first seemed too difficult to obtain. It was at this juncture that a debacle occurred, that has gone down in the history of physics as the ultraviolet catastrophe.

## Ultraviolet Catastrophe

The initial attempt was to treat the atoms of the container walls as a gas, or rather, as a set of vibrating charges (oscillators) each of which has, by virtue of Maxwell's theorem, an average energy $kT$ (one half of this amount is kinetic energy and the other half is potential energy). After this it was possible to calculate thermodynamically the density of radiation in energy units. Lord Rayleigh (the first to derive the formula) assumed that the number of oscillators was proportional to $\nu^2 \Delta\nu$ for each frequency interval. Rayleigh's formula is obtained by counting the number of possible different vibrations of atoms. But difficulties appear in connection with the equipartition theorem. By assigning an energy $kT$ to each oscillator, Rayleigh derived the so-called Rayleigh-Jeans formula for the density of energy in equilibrium with the walls:

$$f(\nu)\,\Delta\nu = \frac{8\pi\nu^2 kT}{c^3}\,\Delta\nu$$

It is worth noting that nowadays we use a new Planck constant $\hbar$ (read *h bar*), $\hbar = h/2\pi$, in order to compensate for the factor $2\pi$ in the frequency formula $\omega = 2\pi\nu$. In this section we follow the old custom of using $\nu$ and $h$.

This formula fits experimental data at low frequencies but, as frequency increases, the number of oscillators increases indefinitely and, if each oscillator is assigned an energy $kT$, the energy of radiation becomes infinite. If the electromagnetic field is treated in terms of the kinetic theory of gases, it proves insatiable, for however large the energy released by the walls, the energy is converted into oscillations at ever higher frequencies. The conclusion obtained in the framework of classical physics is that a thermodynamic equilibrium cannot exist between the walls and the electromagnetic field.

An attempt to remedy the situation was made by Wilhelm Wien. His attention was attracted to a formula for energy distribution in the ultraviolet frequency range and he found that the amount of energy it contains in the frequency interval from $\nu$ to $\nu + \Delta\nu$ fits the following formula quite well:

$$a\nu^3 \exp\left(-\frac{b\nu}{T}\right)\Delta\nu$$

where $a$ and $b$ are some constants. The physical meaning of this formula was unclear, for it had no relation to the kinetic theory and failed at low frequencies. A strange situation had developed. One formula was theoretically sound but led to absurd results; another formula handled the catastrophe well at high frequencies but was patently incorrect at low frequencies. There must have been a flaw in the argument. This flaw was in the foundations of the theory and so logic was powerless to expose it. The logic had to be shattered and this is what Max Planck did.

## A New Fundamental Constant

The key to the mystery was hidden in Wien's distribution formula. It is immediately noticeable that a new constant appears in the exponent: *b*. At the time nobody multiplied temperature by Boltzmann's constant (we have mentioned that it was introduced only by Planck). But if the exponent is written in the form

$$\frac{b\nu}{T}=\frac{bk\nu}{kT}$$

then the formula for distribution will have a new coefficient, i.e. *bk* instead of *b*. The dimensionality of the coefficient *bk* is energy  time. By looking at Wien's formula it was possible to realize at last that there was no way to derive it by any arguments based on equations of classical physics. One had to give up classical physics as hopeless, dump the logic, and invent a new hypothesis without bothering too much at the beginning about what it meant. The hypothesis that served this purpose was the quantum hypothesis.

Planck clearly understood how unusual his hypothesis was. But it was saving physics and that alone gave him sufficient grounds for defending it. The hypothesis assumed that the atoms in the walls of the container with radiation (we called them oscillators) can emit and absorb electromagnetic waves only by discrete portions, that is, by quanta with energy $h\nu$. This assumption proved sufficient for eliminating the ultraviolet catastrophe.

Much later Planck wrote to Wood from Berlin: "Dear colleague! In the course of our pleasant dinner at Trinity Hall you expressed a wish that I write to you in more detail on the psychological state that had led me some time ago to postulating the quantum-energy hypothesis. In what follows I shall try to do my best and satisfy your curiosity. Very briefly, I can describe the whole chain of actions as an outcome of a complete despair. By nature I am a friendly soul, by no means inclined to ambiguous adventures. But for six long years (ever since 1894) I waged a war with the problem of equilibrium between radiation and matter, with no success; I was aware that this problem was of fundamental importance for physics; I knew the formula which gave the distribution of energy in the blackbody spectrum; a theoretical interpretation was to be obtained by all means, whatever the price. Classical physics was of no use here: this was clear because it implied that the energy of matter was converted totally into radiation. To prevent this, it was necessary to introduce a new constant that would take care of the vanishing of energy.

I was prepared to sacrifice my well-established physical concepts. Boltzmann had explained how thermodynamic equilibrium grows from the statistical one; by applying his arguments to the matter-radiation equilibrium it was possible to eliminate the conversion of energy into radiation, by postulating that from the very beginning energy was to be in the form of quanta. This was a purely formal assumption, and actually I did not ponder over it too much, being sure that I must obtain the positive result regardless of consequences or of the price to be paid."

Planck's words call for an explanation. Imagine a container, or a box filled with an electromagnetic field. Let the walls contain electrons which are not free but oscillate as if held by an elastic spring. Do not think that this picture is too crude because the laws of thermal equilibrium are independent of the concrete design of the system, and our model with its electrons must give the same results as any other. But two conditions must be satisfied: first, the oscillation frequencies of electrons must be very different in order that they can emit and absorb any frequency of electromagnetic radiation and, second, the electrons must be in thermal equilibrium with the walls in order that their motion can be described by a definite temperature.

Unfortunately, the derivation of Planck's distribution formula is not an easy matter as it is necessary to calculate the distribution of the oscillators' energies. We choose to give the final result. The formula derived by Planck is

$$f(\nu)=\frac{8\pi h\nu^3}{c^3}\,\frac{1}{\exp\left(\frac{h\nu}{kT}\right)-1}$$

The principal feature of Planck's formula manifests itself in the high-frequency range. Having assumed that energy can be emitted and absorbed only in discrete amounts, that is, in quanta related to the frequency by the formula:

$$\varepsilon=h\nu \quad (=\hbar\omega)$$

Planck observed that the ultraviolet catastrophe dissolved, and he arrived at an acceptable formula for the distribution. At each temperature the spectrum can be divided into two parts: one comprising of frequencies above $kT$, the other of frequencies below $kT$ Roughly speaking, the quantity $kT$ characterizes that part of the spectrum in which most of the energy is concentrated. When $h\nu$ is much greater than $kT$, the exponential function in the denominator becomes large and the unit constant can be neglected. We thus obtain

$$f(\nu)=\frac{8\pi h\nu^3}{c^3}\exp\left(-\frac{h\nu}{kT}\right)$$

and so Planck's formula reproduces the behavior of Wien's distribution. The spectrum of the energy falls off very rapidly as the energy increases so that no "catastrophe" occurs at high frequencies.

The behavior of radiation in the box is such that the oscillations of the electromagnetic field corresponding to high frequencies have practically no energy. This is a corollary of Planck's quantum hypothesis. The classical theory holds that each vibration must have the mean energy $kT$ If $kT \gg h\nu$, this energy corre ponds to several quanta. But if $kT \ll h\nu$, even one quantum is too much. Atomic oscillators cannot emit one fourth or one half of a quantum since these quantities do not exist in nature. And since "large" quanta (quanta with high frequency) are not emitted, they are absent in the electromagnetic field. These degrees of freedom are "frozen out" The frequencies that are "frozen out" are those whose quanta are too large compared with $kT$, As the temperature diminishes, gradually more and more oscillations get “frozen” At absolute zero all degrees of freedom vanish and the energy and entropy of radiation tend to zero.

The effects arising from “freezing out” the degrees of freedom had been actually discovered by Nernst long before quantum mechanics was born, when he tried to deduce how entropy must behave in the vicinity of absolute zero.

As for the low-frequency range ($h\nu \ll kT$), at these frequencies the exponential function in Planck's formula can be replaced by the approximation $e^{\alpha} \approx 1 + \alpha$ if $\alpha \ll 1$, and we obtain the Rayleigh-Jeans formula:

$$f(\nu) = \frac{8\pi\nu^2}{c^3} kT$$

This is a remarkable formula, for it has lost Planck's constant. Hence at low frequencies, when quanta are “small”, the formula gives the classical number of the degrees of freedom for the electromagnetic field, viz. $8\pi\nu^2/c^2$ per frequency interval $\Delta\nu$ since there is one $kT$ of energy per degree of freedom.

Planck's intuition about the quantum is quite outstanding. Indeed, there is no logical sequence that could have led him to the discovery.

Actually Planck did not think in terms of real quanta, the quanta of an electromagnetic field. Quanta for him were merely the portions of energy given away by oscillators. It was five years later that Einstein noticed that if a quantum has an energy, special relativity requires it to have a momentum as well. Quanta must then have an independent existence as particles with energy ε and zero rest mass.

Exact calculations using Planck's formula give the following expression (the Stefan-Boltzmann law) for the density of radiation energy (energy per unit volume), viz.

$$E_0 = aT^4$$

where

$$a = \frac{\pi^2 k^4}{15\hbar^3 c^3} = 1.917 \cdot 10^{-15}\ \text{erg}/(\text{cm}^3 \cdot \text{deg}^4)$$

This formula simultaneously includes the three fundamental constants, $k$, $\hbar$, and $c$. Boltzmann's constant is contributed by the kinetic theory, Planck's constant by quantum mechanics, and the speed of light by Maxwell's theory about the electromagnetic field.

Usually the Stefan-Boltzmann law is written for the energy emitted per second into vacuum by a unit surface of a body heated to a temperature $T$ rather than for energy density. Its usual power is thus:

$$\text{energy flux} = \sigma T^4$$

where

$$\sigma = 5.67 \cdot 10^{-5}\ \text{g}/(\text{cm}^3 \cdot \text{deg}^4)$$

The constants σ and $a$ are related to each other by the formula

$$\sigma = \frac{1}{4} ac$$

By dividing the energy density $E_0$ by the energy of one oscillation, i.e. $kT$, we can obtain a quantity that can be interpreted as the number of quanta per unit volume. It is approximately equal to $14T^3$. Hence, the number of quanta does not remain constant but increases with temperature. This is the principal difference between a gas of photons and an ideal gas containing a constant number of particles.

Planck's discovery was given a physical substance when Einstein realized that an electromagnetic field consists of quanta (photons) and that the oscillators emit and absorb the photons, which are particles moving at the speed of light and having zero rest mass.

Photons entered physics so unexpectedly, and the recognition of their existence was so difficult, that it was only in 1924 that photons were treated as a gas and theorists began to apply the laws of statistical physics to them.

## Photon Gas

In 1924 a young Indian physicist Jagadis Chandra Bose discovered that Planck's distribution can be obtained in almost the same manner as the Maxwell distribution if one assumes that the electromagnetic field is a system of a large number of photons, that is, if it is treated as an ideal photon gas. It must not be ignored, of course, that photons are not ordinary atoms because their rest mass is zero. Bose did keep these in mind and found that Planck's distribution formula is the equilibrium distribution of a photon gas which was later christened "Bose gas".

Bose's derivation pleased Einstein immensely; he translated the paper from English into German and sent it to *Zeitschrift für Physik*. After this the electromagnetic field (field of photons) became an example of a new ideal gas whose equation of state obviously had nothing in common with the Clapeyron-Mendeleev equation.

The derivation of the equation of state for a photon gas is no more complicated than that for an ordinary ideal gas. But it is worth the time to look at it closer.

Right now we only have a formula for the radiation density $E_0$. If the energy density is multiplied by the volume, the result is the internal energy of the radiation:

$$U = aT^4V$$

In order to increment the internal energy by $\Delta U$, the temperature must be increased by a certain amount $\Delta T$, hence

$$U + \Delta U = a\,(T + \Delta T)^4\,V$$

But

$$(T + \Delta T)^4 = T^4\left(1 + \frac{\Delta T}{T}\right)^4 \approx T^4\left(1 + \frac{4\Delta T}{T}\right)$$

whence

$$U + \Delta U = U + 4aT^3V\,\Delta T$$

This means that an increase in energy by $\Delta U$ is related with the increment in temperature $\Delta T$ by the formula

$$\Delta U = 4aT^3V\,\Delta T$$

But the increment in energy when $\Delta T = 1$ is the heat capacity of the system at constant volume, i.e.

$$\Delta U = c_V \, \Delta T$$

hence

$$c_V = 4aT^3V$$

Now we can calculate the change in entropy. We know that

$$\Delta S \quad \frac{\Delta Q}{T} = \frac{c_V \, \Delta T}{T}$$

because the heat supplied to a photon gas is added to its internal energy. We thus find that

$$\Delta S = 4aT^2V \, \Delta T$$

Now it is necessary to make a guess about the formula relating entropy to temperature such that the increment in entropy is given by the above expression.

Assume that the formula for entropy is

$$S = AT^B$$

where the coefficients $A$ and $B$ are the quantities we have to find. We increment $S$ by $\Delta S$ and $T$ by $\Delta T$:

$$S + \Delta S = A\,(T + \Delta T)^B \approx AT^B + ABT^{B-1}\,\Delta T$$

that is

$$\Delta S = ABT^{B-1}\,\Delta T$$

A comparison with the formula for $\Delta S$ we derived earlier immediately gives us

$$B = 3, \quad A = \frac{4}{3} aV$$

We have thus determined the relation between the entropy of the radiation and its temperature, i.e.

$$S = \frac{4}{3} aT^3 V$$

Note that at $T = 0$ the entropy vanishes in accordance with Nernst's results.

It can be shown that radiation behaves as a gas, that it can be compressed by doing work on it, and that on expansion it does work as an ordinary gas. For instance, let the volume, enclosing the radiation, increase from $V_1$ to $V_2$. If the process is reversible and takes place at constant temperature, the entropy of the radiation increases with the volume

$$S_2 - S_1 = \frac{4}{3} aT^3 (V_2 - V_1)$$

An increase in entropy is associated with additional heat, $\Delta S = \Delta Q/T$, hence,

$$\Delta Q = \frac{4}{3} aT^4 (V_2 - V_1)$$

Expansion increases the energy of the radiation by

$$U_2 - U_1 = aT^4 (V_2 - V_1)$$

The increase in energy is evidently less than the amount of heat supplied. This is to be expected because part of the heat went into doing the work.

The last two formulas yield the expression for this work:

$$A = \frac{1}{3} aT^4 (V_2 - V_1)$$

But we know that this work is equal to the product of the gas pressure by the increment in volume, that is,

$$A = p (V_2 - V_1)$$

Hence, the pressure of the radiation is

$$p = \frac{1}{3} aT^4 = \frac{1}{3} \frac{U}{V}$$

This is the equation of state for a photon gas. We notice immediately a drastic difference between it and the equation of state for an ideal gas. The most remarkable fact is that the pressure is independent of the volume, that is, the photon gas can be compressed isothermally without increasing its pressure. This behavior may seem to defy common sense but in fact there is nothing strange in it because the number of photons, as we remember, is not conserved. As the gas is compressed, part of the photons disappear being absorbed by the container's walls and new photons are emitted as the gas expands.

If the entropy of a photon gas is maintained constant, that is, if the process is adiabatic (isentropic), the volume and temperature of the gas are related by the adiabatic equation:

$$T^3 V = \text{const}$$

Knowing the equations of isotherm and adiabat, the reader can verify Carnot's theorem with a photon gas chosen as the working substance.

A photon gas has another peculiar feature: it is almost always ideal. Photons practically never interact (never collide), so that their thermal equilibrium can only be established through absorption and emission by the walls of the container.

If we could create conditions for maintaining an equilibrium photon gas and could measure its pressure, we would have an ideal thermometer that measures absolute temperature and requires no corrections. This would be the most accurate thermometer in the world. Unfortunately, it is very difficult to reproduce Lebedev's experiments (to measure light pressure), and it is even more difficult to maintain such a thermal equilibrium. For these reasons it is not yet feasible to develop a photon thermometer in this pure form, although the principle of the photon thermometer has been used for quite a long time to estimate the temperatures of stars. If the radiation emitted by a star were described by the Stefan-Boltzmann formula, the star would be a thermometer measuring its own temperature. But then it would have to be a blackbody.

## Blackbody

Not every heated body emits a spectrum described by Planck's formula and spectra may be very different. Sometimes they consist of lines, sometimes of bands. For the spectrum of a body to be Planckian, the radiation must be in thermal equilibrium with the emitting body, it must "forget" completely how it was born.

Various models were devised in the last century for this process and the most popular of them was represented by a closed cavity with a tiny hole in the wall. This cavity was called a "blackbody" The radiation was repeatedly reflected by the walls until, like a gas, it gradually attained thermal equilibrium.

In reality it is extremely difficult to formulate which conditions a blackbody must satisfy. To find out whether radiation is thermal, i.e. equilibrium radiation, we have to measure its spectrum: all the conditions are met if the spectrum is Planckian. ("Sufficient unto a blackbody is the spectrum thereof.")

The reader will now appreciate the astonishment of physicists when it was discovered that the whole Universe is filled with a photon gas having a Planckian spectrum. The photons are carrying information about the very distant past of the Universe and give the most impressive proof of its expansion. It had all attributes of a miracle, but the miracle needed deciphering.

## Primordial Background Radiation

This was the problem that arose when Robert Wilson and Arno Pensias discovered weak radiowaves in 1965 that were coming to us from deep space. These signals were observed at a wavelength of 7.35 cm (in the microwave band of the spectrum). If one assumed that this radiation was observed at the maximum of Planck's distribution, the situation looked as if the space was filled with a blackbody radiation at about 3 K. It was immediately suggested that this radiation manifested a remnant of the violent processes that had taken place in the Universe when it had been very hot. Furthermore, it was recalled that George Gamov had predicted the existence of such primordial radiation as early as 1948 but the prediction had been forgotten by 1965.

If we move back in time, the density of matter in the Universe increases and energy increases alongside density. The photons in such hot Universe are created and then disappear, being transformed into electron-positron pairs and all the particles are in thermal equilibrium.

But the Universe expands, and the energies of the particles diminish. This effect can be observed even now. Very distant objects, such as quasars, galaxies, and clusters of galaxies, send us radiation whose wavelengths are shifted to longer wavelengths compared to the same lines in the spectra of the same elements on the Earth (the "red shift"). We conclude, therefore, that the distant objects are receding from us and that the shift of the spectral lines is a result of the Doppler effect. The velocity of recession is proportional to the distance separating us from the luminous object according to the formula $v = HR$, where $H$ is Hubble's constant, which is named after the astronomer who discovered the connection in 1929. The red shift was discovered in 1922 by Vesto Melvin Slipher, whereas Edwin Powell Hubble derived the relation between the velocity of recession and the distance. Hubble's constant is approximately $\frac{1}{1.8 \cdot 10^{10} \text{ years}}$. As the Universe expands, the mean energy of particles decreases and the temperature of the whole heated mixture falls. According to Hubble's law, the radiation wavelength is a linear function of distance, so that wavelengths become longer as the Universe ages. The energy of photons decreases as wavelength increases, and temperature correspondingly diminishes.

Roughly speaking, the temperature of all parts of the system remains the same as long as the energy exchange between quanta and other elements of the world proceeds intensively. But as the Universe cools down and so the matter cools, a moment comes when the photons cannot easily "get rid" of their energy by forming electron-positron pairs. The pair forming requires an energy above 0.5 MeV, or a temperature of $5 \cdot 10^9$ K. Nevertheless, photons can dissipate some energy in collisions with free electrons. However, at still lower temperatures the electrons can join the protons to form hydrogen atoms. Then the large mass of these atoms precludes them from withdrawing any more energy from the photons. The photons then bounce away from the atoms like a tennis ball bounces away from a wall. The Universe has neither walls nor a sufficient number of oscillators to assist the photons in bringing their temperature down to the one corresponding to the temperature of the matter in the Universe. The photons thus find themselves isolated, like nuclei in a lattice. The transformation of the photons into an isolated photon gas takes place at a temperature around 3000 K. During the subsequent cooling the photons lose practically no energy in their interactions but their wavelengths continue to grow in accordance with the expansion of the Universe. This wavelength increases to exactly the same degree as the distance between galaxies increases.

The speed of light remains constant over time and so the frequency of radiation gradually decreases. Hence, the energy of photons, $h\nu$, diminishes with time.

Let us again look at Planck's formula: it includes $h\nu$ in the combination $h\nu/kT$. Consequently, a decrease in $\nu$ gives the same result as a decrease in $T$. Indeed, if $\nu$ and $T$ are reduced by the same factor, the argument in Planck's formula will not change, and Planck's distribution, although unaltered, will refer to a lower temperature. The photon gas is cooling and its temperature diminishes in inverse proportion to the radius of the Universe (or the distance between galaxies), hence

$$T \propto \frac{1}{R}$$

The volume $V$ of the Universe grows proportionally to $R^3$ or to $T^3$, and thus we arrive at a remarkable formula:

$$VT^3 = \text{const}$$

This is an already familiar formula since it describes the adiabatic expansion of a photon gas. The photon gas that fills the Universe expands as if it were in a vast cylinder-and-piston.

First observations did not give enough data to verify the theory because the measurements were only carried out at one wavelength in the range of the maximum. But new measurements confirmed that the spectrum of microwave background indeed fits the Planckian curve quite well on both sides of the maximum.

The temperature corresponding to this curve is 2.75 K and there is no longer any doubt that the cosmic background of microwave radiation is indeed the remnant of the photons that once played their part in the evolution of the Universe.

But even the primordial photon gas is not in an ideal thermal equilibrium. Careful measurements have revealed that Planck's formula describes its spectrum only to within two decimal places. This is caused by the interactions between photons and molecules, the motion of the Earth with respect to the microwave background radiation and some other factors. From the standpoint of thermodynamics the microwave background radiation is thus less ideal than an ideal gas in a laboratory.

It is thus clear that our Universe is a thermostat in which a temperature of 2.75 K is maintained. Measurements of the temperature of the microwave background radiation coming from different areas of the sky show that the velocity of the solar system with respect to the microwave background radiation is approximately 300 km/s. We remind you for comparison that the orbital velocity of the Earth around the Sun is 30 km/s.

The microwave background radiation proved to be very similar to the absolute frame of reference against which the velocity of space bodies can be measured.

It follows from the theory of the evolution of the Universe that there must exist, in addition to the photon background, a neutrino background whose temperature must be slightly lower than that of the photons, around 2 K. So far nobody knows how to detect such "primordial" neutrinos. This is a difficult challenge for future observers.

## Baryonic Asymmetry of the Universe

The number of problems yielding to scientific scrutiny is steadily growing as science progresses. Aspects which have lain unnoticed until now recently have become the subjects of active discussion and "hot" controversy. Among such "hot" issues is the discussion about why the Universe has come to have no (or almost no) antiparticles. All atomic nuclei are built of protons and neutrons, but a huge accelerator had to be built in order to discover (after many years of search) the existence of antiprotons and antineutrons.

Nowadays general agreement exists on what the Universe was like some twenty billion years ago: a tiny system with a fantastically high density and a fantastically high temperature. Everything that we can now observe in the Universe—galaxies, stars, planets, and ultimately Man himself—evolved from this hot and presumably uniform blob. The state of this matter was such that very high energy was concentrated in each degree of freedom, and hence, any sort of particle or antiparticle could be created and then annihilated because neither their masses nor charges were obstacles to their creation. The current opinion of physicists is that at such high energies any type of particle can turn into any other type of particle, and hence we conclude that in this chaos (sometimes called the Ylem) every sort of particle was represented almost equally.

The Ylem was very nearly in a state of thermal equilibrium. This means that it could be assigned some (even if not too accurate) temperature, and we can assume that its entropy was very nearly maximum. It is this last assumption that leads us to the conclusion that the numbers of particles of each different species were (approximately) equal because in maximum entropy conditions every possible state of the system must be mixed. But the example of the radiation has already taught us that such an equilibrium is not always realized. Thus, as the Universe expands, photons break away from matter and, in the sense of their thermal properties, lead an independent life. We recall that this happens when atoms are formed and the energy of each photon becomes so small that the photons are unable to ionize the atoms and thus are unable to exchange further energy with matter.

But having explained the lack of equilibrium between photons and baryons (protons and neutrons), physics was faced with a more formidable problem, that of explaining the excess of baryons over antibaryons. By convention, baryons are assigned a number, similar to electric charge, called the baryon number. A baryon's baryon number is +1, that of an antibaryon is —1, and photons, electrons, and the other sorts of particle are assigned a baryon number of zero. This baryon number is introduced in order to ensure the conservation of the total baryonic "charge" of a system, that is, both protons and neutrons can be created or annihilated only as a pair with their antibaryons. There exist still heavier baryons (denoted by $\Delta$, $\Sigma$, $\Lambda$, $\Xi$) but their number must be vanishingly small at low temperatures since the "population" of high-energy levels, as we know, decreases with decreasing temperature. But what happened to the antibaryons that were as abundant as baryons in the original thermal equilibrium?

Indeed, the masses of particles and antiparticles should be exactly equal, and thermal processes should never shift the equilibrium between them. But if the equilibrium did shift, it means that some nonequilibrium process must have been at work.

The characteristics of the process that was required to eliminate antibaryons were formulated fairly long ago and already at that time a serious discussion had begun about the processes which took place during the early stages of the evolution of the Universe.

The main effect that should have been realized was the nonconservation of the baryons number, i.e. antibaryons had to disappear by being converted, for instance, into electrons and neutrinos (and possibly, a host of other particles). This was hardly an acceptable explanation.

Moreover, in order that antibaryons could disappear more often than they were created implied that there were some important processes that are asymmetric over time. In quantum mechanics this property is called the violation of time parity (or simply $T$-parity violation).

And finally, in order to prevent thermal equilibrium forever, it is necessary that the relevant interaction weakens over time or as the Universe expands so that the products of the decay of antibaryons could never "reassemble" into antibaryons. We shall recall here what has been said about the independence of the Maxwell distribution on the properties of walls (i.e. on the law of the interaction between the atoms of a gas and the wall). We have seen that the law governing the reflection of atoms against the walls of the container does not affect the distribution, the law only determines the time over which thermal equilibrium is attained. Similarly, even with *T*-parity violated, antibaryons could not leave the scene if their interaction with other particles was not somehow switched off.

It is most remarkable that all these properties were indeed found in the world of elementary particles. The most important factor was the reconciliation of the theory with the idea of the non-conservation of the baryon number and, in particular, with the idea of proton decay. This effect, which probably has already been observed (though the experiments are still too few for certainty), is predicted by our current theories which postulate that during the early stages of the Universe every interaction was equally probable, the proton being able, for example, to transform itself into light particles without any difficulty. At the present time, however, this interaction is very feeble and proton decay became a very rare event: theoretical estimates give a proton a lifetime of more than $10^{30}$ years.

This property of the proton can be described as follows: the probability of proton decay depends on the proton radius, which constantly fluctuates around its mean value, $10^{-13}$ cm. When (very infrequently) a proton contracts to about $10^{-30}$ cm, the probability of decay becomes large and it decays. Evidently, this process is very rare, and for this reason it has not yet been detected. Fortunately, the number of protons is very large, so that the duration of the experiments need only be several months. The detection of a proton's decay is therefore extremely difficult but nevertheless may prove to be feasible. The first experimental indications that it is a real event have been found recently.

Another possibility of proton decay was suggested by V. A. Rubakov. He concluded that a proton should decay if it collides with the hypothetical Polyakov-'t Hooft monopole; monopoles, if they exist, are now distributed throughout the Universe with very low density but during the early stages of the Universe their density was large. Correspondingly, the decays of baryons were frequent in the young world and are almost nonexistent in our time.

If proton decay is confirmed, all the rest of the theory will go smoothly. The violation of *T*-parity was found a long time ago (in the decays of K-mesons), and the weakening of the interaction over time or distance is an important link in the modern theory that must unite all the interactions in the Universe (the so-called Grand Unification Theory, or GUT).

The story recounted above is certainly only tenuously related to temperature but nevertheless it is conclusive evidence of the unified picture into which science knits the most remote elements of our world and shows how familiar physical concepts cross into new areas about which, as we mentioned on other occasions, former generations of physicists could not even guess.

## Black Holes

The temperature of the primordial microwave background radiation is not the most striking exhibit in our exhibition of temperatures. The story of the temperature of black holes is an even more fantastic case.

Our next story began very unexpectedly in the 18th century. In 1783 a young British physicist, John Michell, noticed that if a star had a very large radius (500 times the solar radius) and a density equal to that of the Sun, then "...the light emitted by this body would be returned back owing to its weight." Somewhat later Marquis Pierre Simon Laplace repeated this conclusion (in 1799). The prediction, which is based on some almost correct (though incorrectly derived) formulas, was borne out by Einstein's general relativity.

The formula that gives the radius of the star for which the escape velocity equals the speed of light (so that no body, or even light, can leave its surface) is

$$R_{gr} = \frac{8\pi}{3}\frac{G\rho}{c^2}$$

where $G$ is Newton's gravitational constant, and $\rho$ is the density of the star. If we introduce the mass of the body (the star)

$$M = \frac{4}{3}\pi R^3\rho$$

the formula for $R_{\text{gr}}$ can be rewritten as a mass-radius relation:

$$R_{\text{gr}} = \frac{2GM}{c^2}$$

This quantity is called the gravitational radius of the body. It is proportional to its mass, and for the Sun is equal to 3 km.

Strange events take place around a cosmic object whose radius $R$ does not exceed its gravitational radius $R_{\text{gr}}$. Every object in the immediate vicinity of such a celestial body (a distance less than $3R_{\text{gr}}$ if the body's velocity is not large) falls onto its surface and can never break loose because of its tremendous gravitational field. A macabre name was chosen for such an object, "black hole", because neither signals nor particles can escape from the surface of a black hole.

The strong gravitational field of a black hole affects the frequency of photons. At a distance $R_{\text{gr}}$ from the center of a black hole the frequency (and the energy) of a photon drops to zero. It is as if a photon in trying to escape from the gravitational pull of the black hole must spend all its energy and "emerges" at zero energy, that is, it simply vanishes. Strange things happen to bodies falling on the black hole. Their fall itself releases vast energy, and this fact makes the black-hole hypothesis extremely attractive to astrophysics.

Black holes may be at work in those regions of the Universe where very much energy is being liberated, i.e. quasars and the nuclei of galaxies. So far nobody knows where this energy comes from. These objects may draw most of their energy from black holes which may have masses that are millions and billions of the solar mass and which "burn", as atom bombs do, the rest energy of an object falling into them in accordance with the formula $E = Mc^2$. This picture of energy balance looks quite impressive. There are reasons to believe that the binary star X-1 in the Cygnus has a black hole as an invisible companion. All these assertions, however, are not yet sufficiently reliable to deserve a more detailed discussion.

## Black-Hole Paradox

The very existence of a black hole is a paradox itself. A black hole behaves like a body at absolute zero because the black hole can completely convert heat into work.

When a body falls into a black hole, it can do work at the expense of the gravitational attraction to the black hole. The energy of a body falling into a black hole, together with its "rest energy" $M_0c^2$ ($M_0$ being the rest mass of the body), can be converted into work (this work is realized as a powerful emission of electromagnetic and gravitational waves).

At the boundary of a black hole the total energy of the body is therefore zero. It can be said that the rest mass of the body is cancelled out by the negative potential energy of this body in the gravitational field of the black hole. In ordinary terrestrial conditions the potential energy is very small in comparison with the rest energy so that the mass of a falling stone remains practically unaltered; but a fall onto a black hole reduces an object's mass to zero.

The law of gravitation is such that the attractive force is proportional to the mass of the attracted body regardless of what creates this mass. A hot kettle is slightly heavier than a cold one and so a hot kettle falling onto a black hole will release slightly more energy ($U/c^2$ more, where $U$ is the internal energy) than a cold one. A black hole acts as an ideal heat sink at $T = 0$ K, and no energy can be extracted from it by any means. This means that the efficiency of a cycle using a black hole as a heat sink is, according to Carnot, equal to unity. This creates a situation that very much resembles a perpetual motion machine of the second kind, with the Nernst heat theorem definitely violated. This paradox inevitably points to the impossibility for a black hole to be at absolute zero.

The resolution of this paradox must be sought in the thermodynamics of black holes. The first guess was as follows.

If the temperature of a black hole is not absolute zero, the black hole must possess entropy as well. If the black hole is spherically symmetrical, does not rotate, and is not charged, its entropy can only depend on the hole's mass. But entropy is a dimensionless quantity, it is not affected by the choice of units of measurement, whilst the numerical value of mass is obviously determined by some sort of unit, whether we measure it in grams or millions of tons. The entropy of an ideal gas was determined by the ratio of volumes and the ratio of temperatures. Presumably, the entropy of a black hole could also be determined by the ratio of its mass to some reference mass. But which reference mass? And what should the expression for a black hole's entropy be?

A qualitative solution of the problem was found by J. D. Bekenstein. His attention was drawn to one of the theorems arising out of general relativity. The theorem stated that regardless of the particulars of processes taking place in a system containing black holes, the total surface area of the black holes can only increase. This very general theorem is reminiscent of the theorem about the increase in entropy. Both area and entropy are additive quantities, and both depend on the mass of the black hole. There was a temptation, therefore, to postulate that the entropy of a black hole is simply proportional to its surface area $A$: $S \propto A$. But how to make entropy dimensionless if area $A$ has the dimensionality of length squared?

## Planck's Units

The world of elementary particles has no scale of lengths. The two constants $\hbar$ and $c$ cannot be combined to form a quantity with the dimensionality of length or time. One has to add mass. Then, for instance, $\hbar/mc$ gives length.

General relativity also has no length scale because it cannot be composed out of $G$ and $c$. But length can be obtained with the help of mass: $Gm/c^2$.

Now let us combine both lengths $\hbar/mc$ and $Gm/c^2$ into their geometric mean: $(\hbar G/c^3)^{1/2}$.

This eliminates mass. This is the unit of length that was proposed by Planck.

After Planck had introduced the two fundamental constants $\hbar$ and $k$, he noticed that it was possible to construct a new system of units not tied to any artificial references. They are:

length $l_P = \left(\frac{G\hbar}{c^3}\right)^{1/2} = 5.110 \cdot 10^{-33}$ cm

time $t_P = \left(\frac{G\hbar}{c^5}\right)^{1/2} = 1.7016 \cdot 10^{-43}$ s

mass $m_P = \left(\frac{\hbar c}{G}\right)^{1/2} = 6.189 \cdot 10^{-5}$ g

frequency $\omega_P = \left(\frac{c^5}{\hbar G}\right)^{1/2} = 0.5863 \cdot 10^{43}$ $s^{-1}$

energy $\varepsilon_P = \left(\frac{\hbar c^5}{G}\right)^{1/2} = 0.5563 \cdot 10^{15}$ ergs

temperature $T_P = \frac{1}{k}\left(\frac{\hbar c^5}{G}\right)^{1/2} = 4.029 \cdot 10^{31}$ K

Planck's units are convenient for calculations of systems in which both quantum and gravitational effects are important.

But Planck's units are not only convenient, they possess at the same time a distinct advantage. Their existence signifies that nature, that is, the Universe, works with natural scales related simultaneously both to the quantum and to the relativistic properties of the world. Planck's constant established the relation between energy and frequency (the quantum scale), and the speed of light established the relation between mass and energy (the energy scale). It seems natural to assume that Planck's units also define scales for the parameters of certain events or objects. A black hole (and its entropy) appears to be an excellent candidate for the application of Planck's units.

Let us assume that the entropy scale is related to a constant length $l_P$, that is, that the surface area of a black hole can be divided by $l_P^2$ to yield a coefficient that cannot be guessed beforehand. Such were the arguments, and frankly they are not too stringent, that were the basis for a hypothesis that the entropy of a black hole must be

$$S = \frac{\alpha A}{l_P^2}$$

where the coefficient $\alpha$ must be calculated by applying some special arguments. This conjecture proved correct. The coefficient $\alpha$ was later calculated by Steven Hawking and he proved that $\alpha = \frac{1}{4}$.

Knowing the entropy, we can calculate the temperature. Replace the area $A$ with its expression via the gravitational radius,

$$A = 4\pi R_{gr}^2 = \frac{16\pi G M^2}{c^4}$$

The formula for entropy in Planck's units then takes the form

$$S = 16\pi\alpha \left(\frac{M}{m_P}\right)^2$$

The expression for temperature is

$$T = \frac{1}{32\pi\alpha} \frac{m_P}{M} T_P$$

By eliminating the mass from these formulas, we find

$$ST^2 = \frac{1}{16\pi} T_P^2 = \text{const}$$

This equation of state is not like anything we know. It states that entropy is lower the greater the temperature and that entropy becomes infinite at absolute zero.

We conclude, therefore, that either our line of reasoning includes a blatant mistake or that something tragic happens to the black hole and that it cannot "live up" to absolute zero. However, this paradox could not be resolved in the framework of classical physics.

## Emission of Radiation from a Black Hole

The paradox disappeared when Hawking proved theoretically that particles are created in the neighborhood of a black hole. It was discovered unexpectedly that the theorem about the increase in the surface area of a black hole is invalidated by quantum mechanics and that the entropy of a black hole can be reduced by a flux of photons which are created around a black hole and carry its entropy away.

A very high potential of the gravitational field around a black hole results in the creation of photon pairs (and pairs of other particles) on its surface. The energy of these photons (like that of all particles close to a black hole) is zero, so that they can be created "out of nothing" without violating the law of the conservation of energy. After a pair of photons has been created, one of them sinks into the black hole (without being too rigorous, we can say that the photons that sink into a black hole acquire negative (potential) energy), and the second photon flies away to infinity at the expense of the released energy. The system works like a pulley, one weight is lowered while another one is hoisted at its expense. As a result of this process the black hole's mass is reduced (as well as its surface area) in relation to the energy of emitted photons.

The theory of this effect is extremely complicated but the result is very interesting. A black hole emits photons whose spectrum coincides with the Planckian spectrum corresponding to a temperature (in Planck's units, i.e. $m_P = 1$ and $T_P = 1$):

$$T = \frac{1}{8\pi}\frac{1}{M}$$

This formula gives $\alpha = \frac{1}{4}$.

A black hole thus emits radiation like an ideal blackbody.

## Death of a Black Hole

Now the source of the paradox becomes clear. A black hole is not in equilibrium, it is an unstable system and therefore the notion of its temperature is not strictly correct. As the mass of a black hole diminishes, its temperature increases; the creation of the pairs reduces the mass and thus increases the temperature. As the temperature rises, the intensity of radiation is intensified, thereby increasing the temperature still more. In the long run a black hole must burn out, and in a finite time.

The duration of the burning is readily calculable. By making the scheme somewhat cruder, we can use the Stefan-Boltzmann formula for the emission from a unit surface area of a black hole and multiply the result by the total surface area.

The result is as follows. The lifetime (in seconds) of a black hole with mass $M$ (in grams) is

$$\tau = 2 \cdot 10^{-27} M^3$$

This formula shows that for $M = 10^{15}$ g the lifetime $\tau = 2 \cdot 10^{18}$ s, roughly equal to the age of the Universe. The lifetime increases for the more massive black holes.

Black holes with masses of about one solar mass ($10^{33}$ g) can be said to live indefinitely. The temperature of such black holes must be very low. Rewriting the formula for temperature in the form

$$T = \frac{10^{26}}{M\ (\text{g})}$$

we find that for $M = 10^{33}$ g the temperature is $10^{-7}$ K.

The temperature is practically equal to absolute zero for all surviving black holes, and especially for the hypothetical gigantic black holes that allegedly supply energy to the whole

Universe. These objects emit nothing, and they constitute ideal heat sinks that permit the realization of the ideal Carnot cycle with an efficiency very close to unity.

The story of the black hole is very instructive. The purely theoretical behavior of the black hole contradicted the laws of thermodynamics and the solution was provided by quantum mechanics. The same happened to the third law postulated by Nernst. Only after Boltzmann's formula and quantum mechanics had appeared, did it become clear how the third law was related to the fundamental laws of physics.

The laws reigning in the microscopic world were found to be mandatory for the explanation of phenomena that seemed to belong to the realm of the macroscopic world. The interrelations between different fields of physics are so strong that it is almost impossible to change something in one of them without violating the harmony of the whole physical picture of the world. This is why the attempts to correct general relativity or supplement quantum mechanics have invariably failed. All that we know about physics in our world demonstrates the inevitability of these theories.

## A New Paradox

Black holes less massive than $10^{15}$ g should have burnt out long ago and we do not yet know whether more massive black holes in fact exist.

The theoretical properties of black holes are so unexpected that it is interesting to trace the fate of a small-mass black hole.

The emission of photons carries away both mass and entropy, the temperature of a black hole thereby increasing. Consider a black hole with a mass of $10^{15}$ g. This mass corresponds to a temperature of $10^{11}$ K. At this temperature the energy of the photons is of the order of $kT \cong 10$ MeV Such photons can create electron-positron pairs (the mass of one such pair corresponds to an energy of about 1 MeV). When the mass of the black hole diminishes a thousandfold and the energy of the photons correspondingly increases a thousandfold, the creation of heavy particles will start. With a mass of about $10^{12}$ g, the radius of the black hole will be approximately $3 \cdot 10^{-14}$ cm, that is, roughly equal to the radius of elementary particles. But this is an insidious trap. When the black hole was still big, it mostly consisted of nucleons, that is, protons and neutrons. But the number of nucleons must be conserved (as must the number of electrons) and in counting particles the particle-antiparticle pairs are dropped. Nucleons are said to have a nucleon number of unity, and antinucleons a nuclear number of minus unity. Then the conservation of the number of nucleons is formulated as the conservation of the baryon number:

$$N\ (\text{nucleons}) - N\ (\text{antinucleons}) = \text{baryon number}$$

As a black hole burns out, reducing in size, it cannot affect the number of nucleons. The system $10^{-14}$ cm in size must have room for the same number of nucleons that were contained in the $10^{15}$ g star.

This appears unacceptable but the disappearance of nucleons is even less acceptable. Were the baryon number not conserved, there would be no problem. Should a black hole burn out, thereby reducing the baryon number of the Universe, the black hole would be a mechanism that "converts" heavy particles into radiation. This solution seems strange.

But if the baryon number is conserved, we cannot understand what the fate of the remainder of a black hole with its gigantic baryon number and small mass should be. The properties of this system will not become clear without some radically new ideas.

The key problem is thus the conservation of the baryon number and, hence, the stability of the proton, which we discussed in earlier sections.

Thermodynamics, when applied to black holes, thus led us to new, very profound problems.

## Cooling of Antiproton Beams

The concept of temperature was used unexpectedly and brilliantly in an idea of how to produce proton and antiproton beams that was suggested by Gersh Itskovich Budker.

A long time ago Fermi, when discussing the origin of cosmic rays, considered the probability that charged particles might be accelerated by irregular magnetic fields in cosmic space. This is what Fermi wrote in the relevant paper: "We now consider a fast particle moving among such wandering magnetic fields. If the particle is a proton having a few GeV energy, it will spiral around the lines of force with a radius of the order of $10^{12}$ cm until it "collides" against an irregularity in a cosmic field and so is reflected, undergoing some kind of irregular motion. On a collision both a gain or a loss of energy may take place. A gain of energy, however, will be more probable than a loss. This can be understood most easily by observing that ultimately statistical equilibrium should be established between the degrees of freedom of the wandering fields and the degrees of freedom of the particle. Equipartition evidently corresponds to an unbelievably high energy. The essential limitation, therefore, is not the ceiling of energy that can be attained but rather the rate at which energy is acquired... ." In the ideal case, the energy of a proton would have to reach the energy of the whole enormously large magnetic cloud. This is clearly impossible.

Further on in the paper, Fermi discusses reasons for which statistical thermal equilibrium cannot be attained. It can be said that heat transfer from the random fields to the protons must be extremely slow, but the direction of the energy flux from the fields to the protons is established beyond doubt. A beautiful argument, based on an analogy with the levelling-off of temperature, enabled Fermi to obtain rather simply a qualitative solution of a difficult problem.

Similar arguments led Budker to the idea that has been confirmed by experiment. A beam of antiprotons generated by an accelerator consists of particles whose momenta have a certain spread of directions. This points to some randomly distributed transverse momentum, the width of this distribution being rather large. This spread must be reduced. The momentum along the beam direction (longitudinal momentum) is also somewhat variable but right now this aspect is of no interest because the longitudinal spread is masked by the highly ordered momentum of the particles in the beam.

The distribution of the transverse momenta can be characterized by a parameter similar to temperature. The greater the spread, the higher the "transverse" temperature of the beam.

The idea was to send an electron beam along with an antiproton beam, to mix these beams. It is possible to produce electron beams with a very narrow spread of transverse momenta, that is, with a low "transverse" temperature. But if the electrons have a narrow spread of momenta, they are in a better ordered state (this is equivalent to saying that they have a low transverse temperature, while the heavy particles have a greater spread and correspondingly higher temperature) and a heat flux from the antiprotons to the electrons will appear. The antiproton beam will then "cool down", while the electron beam will "warm up" The spread in the transverse velocities of the antiprotons will be reduced. This conclusion could be drawn without considering at all the details of the interactions between the antiprotons and the electrons.

This method of collimating antiproton beams looks quite promising. In the case of proton beams this method of cooling may considerably simplify the collimation of "good" beams, and in the case of antiproton beams cooling seems to be the only way to forming a beam suitable for experiments.

Budker's "refrigerator" is the most remarkable refrigerator we know of.

## Temperature and Variance

The application of the concept of temperature to such unusual systems as particles in cosmic rays or beams of particles emerging from accelerators is obviously a very elegant idea, but it suffers from one defect. The systems actually have no temperature, as we cannot speak of a temperature in a crowd emerging from a stadium after a football match. Temperature is a characteristic of a system in thermal equilibrium. We know that not all the particles (not all the degrees of freedom) have identical energy in thermal equilibrium. Quite the opposite, the values of the energy of particles are spread around a mean value. This spread has already been mentioned and is characterized by a special quantity, called the variance or $\delta(\varepsilon)$. The variance is proportional to the system's temperature. We can even say that the variance can serve as a measure of temperature. However, what is true for a system in thermal equilibrium is not necessarily true in nonequilibrium cases.

The spread of particle energies in the beam can indeed be described by its variance, but strictly speaking this variance is not equivalent to a temperature. Nevertheless, the statement that energy is transferred from a system with a large energy spread (large variance) to a system with a smaller variance is correct in most cases. It can be shown that this process increases entropy, and entropy is the only factor controlling the direction of thermal processes in nature. For this reason we can use the term "temperature" instead of "variance" and not be afraid of making a mistake. But this is by no means a universal recipe. If two systems have equal variances but are not in thermal equilibrium (or at least one of them is not), a heat flux between them is still possible. This could not happen if their temperatures were equal. What about the direction in which energy will flow? This question can be answered only after the change in entropy is calculated. Energy will be transferred so as to increase entropy. Processes are controlled by entropy and in this sense the concept of temperature is not as general as that of entropy. It should also be noted that similar remarks should have been made when discussing negative temperatures and the nonequilibrium populations of energy levels.

## Brownian Movement

The reader should not be surprised any more by different temperatures coexisting in the same volume. Heat (or entropy) flows from spins to the lattice, from magnetic clouds to a proton, and numerous other examples illustrate the processes of thermal equilibrium when heat is transferred from a more disordered system (higher $T$) to a less disordered system (lower $T$). The first example, historically, of this process was Brownian movement. It was discovered in 1827 by the Scottish botanist Robert Brown who described the chaotic movements of tiny dust particles in a liquid that could be observed through a high-power microscope in a paper in 1828.

It is interesting to recall that almost immediately these movements were associated with the motions of the molecules of liquids, but later this viewpoint was for some obscure reason rejected, and even at the beginning of this century Brownian movement was attributed to flows in the liquid.

The following words can be found in the Russian Brockhaus and Efron Encyclopaedic Dictionary printed in 1905: "For a long time it was believed that the phenomenon was caused by actual molecular movements in the liquid. Mr. Wiener supported this interpretation as early as 1863, but contradicting explanations of the causes of this phenomenon were proposed immediately after the discovery... ." People thus preferred to ignore the problem of Brownian movement. Consequently, when Einstein published in 1905 his paper "On the Movement of Particles Suspended in a Nonmoving Liquid", he did not even refer to Brownian movement. The theory of Brownian movement as such was only presented in a paper published the following year.

The essence of Brownian movement is that in thermal equilibrium (in the framework of the classical kinetic theory of gases) every degree of freedom is equally subject to the law of equipartition.

Dust particles in a liquid form a system, namely, an ideal gas of particles which, though they do not interact among themselves, do interact with the particles of the liquid in which they float.

Imagine that all these particles are at rest. This would mean that the temperature of the "gas" of dust particles were zero. This would inevitably result in a heat flux from the liquid to the dust which would continue until each of the dust particles' degrees of freedom had accumulated energy $\frac{1}{2}kT$. The dust particles will therefore be in thermal motion together with the particles of the liquid.

By considering a dust particle to be a sphere with radius $r_0$ moving in a liquid with viscosity coefficient $\eta$, Einstein derived a formula for the mean square of the particle's displacement, viz.

$$\langle\Delta^2\rangle_{\mathrm{m}} = \frac{kT}{8\pi\eta r_0}\, t$$

where $t$ is time. Even before his work on the theory of Brownian movement, Einstein had noticed that it is possible to determine the Avogadro number by observing the motion of dissolved molecules in the liquid (i.e. by measuring the diffusion coefficient). This means that one has to find $k$ from an experiment and use the known value of the gas constant, $N_{\mathrm{A}} = R/k$. Einstein did precisely this and the estimate he obtained, $N_{\mathrm{A}} = 3{,}3\cdot 10^{23}$, was very close to the value accepted at that time. Einstein's calculation was conclusive evidence of the reality of molecules; this reality was very much in doubt in 1905 for many scientists. It will be useful to remark that the mean displacement of a dust particle is the mean over time calculated for one particle. As we already know, Einstein used the mean over time for one particle and not the mean for an ensemble of particles, as was typical for the kinetic theory of gases at the time. By using this stratagem, Einstein was able to solve the problem.

The formula for the mean square displacement shows that by measuring the displacement of a dust particle it is possible to determine the temperature of the liquid. In principle, this is a very promising method. Dust particles form an ideal gas, and the thermal equilibrium is established quite rapidly. The difficulty lies in measuring $\Delta^2$ with the requisite accuracy.

Other examples, of Brownian movement can be mentioned. For instance, instead of a dust particle, we can consider a sphere with radius $r_0$ that cannot only move translationally but can also rotate. It is possible to calculate the mean square angle of rotation of the sphere around its axis, $\langle\theta^2\rangle_{\mathrm{m}}$. Einstein derived the following formula:

$$\langle\theta^2\rangle_{\mathrm{m}} = \frac{kT}{4\pi\eta r_0^3} t$$

The sphere can serve as a thermometer, and we do not even need to know the value of $k$ to measure the ratio of temperatures.

A similar formula is readily obtained for a sphere fixed to a weightless spring with elasticity coefficient $\alpha$. By equating the mean potential energy of the sphere, as was done for a particle of a gas, to the familiar quantity $\frac{1}{2}kT$,

$$\frac{\alpha}{2}\langle x^2\rangle_{\mathrm{m}}=\frac{1}{2}kT$$

we obtain for the mean square displacement $\langle x^2\rangle_{\mathrm{m}} = kT/\alpha$. Fix a scale alongside the sphere, and you have a thermometer.

## Fluctuations

In our discussion of temperature and entropy we have kept to the outlook of the thermodynamics of the last century. It was assumed that these quantities have strictly fixed values at each point and that the temperature and pressure in a thermal equilibrium are absolutely constant throughout the volume. These assumptions were at the foundation of the first and second laws of thermodynamics.

In reality all the quantities vary with time and coordinates. When deriving the formula for the pressure exerted by a gas on a wall, we meant the mean pressure. If we could monitor the pressure better, i.e. by measuring it every $\tau$ seconds (with $\tau$ so small that the number of impacts against the wall during $\tau$ is not large), the instrument would show that the pressure constantly fluctuates. Pressure is proportional to energy density, so that energy will also change.

Fluctuations of energy (as well as of other quantities) would be best characterized by deviations from the mean value, i.e. $(\varepsilon - \varepsilon_0)_m$. But taken on average this difference vanishes (the deviations to the lower values cancel out the deviations to the higher values). It is therefore natural to characterize fluctuations by the mean square of this quantity:

$$\delta(\varepsilon^2) = \langle(\varepsilon - \varepsilon_m)^2\rangle_m = \langle\varepsilon^2\rangle_m - \langle\varepsilon\rangle_m^2$$

This quantity is called the mean-square fluctuation. It is the quantity usually meant when fluctuations are discussed. It is never easy to calculate fluctuations and we shall give only a few final results.

The formula for pressure fluctuations is

$$\delta(p^2) = \frac{c_p}{c_V}\frac{p^2}{N}$$

or

$$\frac{\delta(p^2)}{p^2} = \frac{c_p}{c_V}\frac{1}{N}$$

where $N$ is the number of particles in the system. This is also an estimate of the accuracy of the concept of pressure as such. Usually $N$ is very large so that pressure fluctuations are extremely small. A similar formula for temperature fluctuations in a monatomic gas is

$$\frac{\delta(T^2)}{T^2} = \frac{3}{2}\frac{1}{N}$$

Such formulas show the accuracy of thermodynamic concepts in ordinary conditions. These two formulas for the fluctuations of pressure and temperature are almost identical. Both state that the accuracy improves as the number of particles increases, being inversely proportional to the square root of $N$:

$$\frac{\delta(p^2)}{p^2} \propto \frac{\delta(T^2)}{T^2} \propto \frac{1}{N}$$

Thus, in 1 mm$^3$ of a gas (at a pressure of 1020 hectopascals) $N \approx 10^{16}$, the relative fluctuations are approximately equal to $10^{-16}$. Consequently, pressure and temperature are sufficiently exact concepts for this amount of gas.

But this discussion of fluctuations was started not only in order to confirm our habitual concepts but also to find a method for measuring temperature. In this sense the formulas given above add nothing because it is very difficult to measure fluctuations in thermodynamic quantities. The problem is somewhat simplified if we consider electrical quantities.

There is no current in an electric circuit which has no e.m.f. At any rate, this is what Ohm's law states. In reality this is not quite true, or rather, it is true only at absolute zero when fluctuations vanish. At other temperatures an electric current can appear accidentally when the thermal motion of electrons becomes accidentally ordered.

Electric-current fluctuations were calculated in 1927 by Harry Nyquist. Obviously, the current that appears cannot be a direct current, and different frequencies of ac current appear with different probability. Instead of speaking of current, we can consider it in terms of e.m.f.

fluctuations. At a frequency $\omega$ such that $\hbar\omega \ll kT$, this e.m.f. is given by the formula

$$\langle \varepsilon_{\omega}^{2} \rangle_{\mathrm{m}} = \frac{T}{\pi} R(\omega)$$

where $R(\omega)$ is the resistance of the circuit at a frequency $\omega$. The e.m.f. fluctuation can also be interpreted as evidence of thermal oscillations in an electromagnetic system. The above formula can already serve as a basis for measuring temperature. However, physicists who are occupied developing a temperature scale devised a still better way.

In order to understand what is to follow, an explanation of noise, or rather white noise, is necessary.

Let us return to a conductor at a temperature $T$ Assume now that a current passes through it and feeds, for instance, the magnetizing coils of an acoustic device; this is the simplest circuit in a telephone line. Thermal effects will superpose some spurious ac currents onto the current carrying the useful information. These currents, passing through the transducer, will produce a noise background. This noise can be represented by a spectrum of signal intensity as a function of frequency. If this spectrum corresponds to random signals, the noise is called white noise; white noise carries no information except that about temperature. Noise accompanies all electromagnetic phenomena. It is not mandatory to transform noise through an acoustic transducer and perceive it as sound. Fluctuations of any physical quantity are referred to as noise, and white noise is just one in particular. By choosing among different phenomena we can finally select an ideal (from the standpoint of theory, at any rate) method of measuring temperature.

Unfortunately, the noise measuring technique, like several other modern precision techniques, is described by a complicated theory, and I shall mention only as an example that by measuring the noise at Josephson junctions (two superconductors separated by a thin layer of insulator) it has proved possible to measure the melting point of helium to five decimal places on the absolute scale.

## Maxwell's Imp

We shall add to this story one more paradox which was the subject of numerous discussions for many years and which tests the "strength" of statistical physics and its relation to the second law of thermodynamics. In thermodynamics everything was clear: the direction of processes is such that entropy inevitably increases, and there is no way to violate this law. But if the atoms and molecules of matter are regarded as material points governed by the laws of mechanics, then the validity of the law of increasing entropy becomes, to say the least, doubtful. If it is possible to mix some atoms moving at high velocities (high temperature) with a number of atoms moving slowly (low temperature) and obtain a system of atoms whose motion can be described by the Maxwell distribution of some medium temperature, why then is it impossible to invent the procedure, that is, somehow separate the slow and fast atoms? This venture would in no way contradict mechanics. Can mechanics provide the means for bypassing the second law of thermodynamics?

The problem is best clarified by inviting the help of Maxwell's imp.

Imagine a minute being that is able to see atoms. Let us put this imp into a gas-filled box and, having arranged on one wall of the box a tiny hole with a door, train this imp to be the doorman so that he opens the door when a fast atom approaches it and let it escape, and closes the door to a slow atom. The decision as to which atoms are fast and which are slow is left to the imp. We only endow it with the ability of measuring very rapidly the velocity of the approaching atoms. After some time we find that the mean velocity of the atoms in the box has been diminished, that is, the gas has cooled down. The imp's work has given the required result.

However, this result does not really disagree with thermodynamics either. Were we to open the door without the help of the doorman, the fast-moving atoms would escape in greater numbers anyway because they come to the opening more often whilst the atoms moving at very low velocities would not reach the door at all. A gas expanding into a vacuum cools down; we know this from thermodynamics.

A new result will be obtained if we change the instructions given to the doorman. The door is to be opened for the slow atoms and closed to the fast atoms. Then the gas will start heating up. The first set of instructions seemed admissible; why not the second?

By employing an imp we thus can devise a simple heating device that consumes no energy. This device would separate a gas into two parts at different temperatures, with the same total energy. This perpetual motion machine of the second kind is just as good as a "conventional" perpetual motion machine. It has the same shortcoming, unfortunately: it cannot be constructed.

The difficulty obviously lies with the imp, and some of its gifts contradict the laws of physics. The paradox was resolved by Leo Szilard in 1928.

First we want to find out what the size of the imp should be compared with the size of molecules (or atoms).

If the imp consisted of a single or a few molecules, it would be subject to Brownian movement itself, and in that sort of frame of reference (whose velocity would change chaotically) it would be unable to measure the velocities of the approaching molecules and unable to stay by the door all the time to open and close it at the right moments. Hence, the imp must be small and heavy, practically immovable from his post. But then we are in for another complication, for the impacts of the molecules will not be able to shift the imp, and it will have to operate with a very light device capable of sensing these impacts, and of measuring velocities; for instance, a light plate suspended with a thread would do. But what should the size of the plate be? A very small one would not stay fixed, and.... The chain of arguments repeats itself all over.

For the imp to carry out its functions, we would have to keep it or its measuring device at a very low temperature, for instance, by cooling it with liquid hydrogen. Then its own thermal movements would stop and it would be able to measure the molecules' velocities. However, counting individual molecules would not be necessary, the imp could monitor fluctuations in the heat fluxes, opening the door when fluctuations slightly raised the temperature.

In this way the imp could, in principle, extract energy from the random motion of molecules, but we would gain exactly nothing. The energy spent on cooling the imp itself, on suppressing its fluctuations (its Brownian movement) would be at least equal to the energy "earned" by the doorman. In serious terms, this means that the instrument for extracting energy from fluctuations cannot be either molecular or macroscopic in size. In both cases it could yield no practical gain.

In our world information is obtained only by spending some energy.

The second law of thermodynamics cannot be violated. This is one of the most powerful laws in our world. It cannot be bypassed in electric circuits either. How attractive it would be to obtain energy by harnessing in a closed circuit the current arising out of chaos. Here a simple electric stove, heating proportionally to the square of electric current (in accordance with the Joule-Lenz law), would operate like the imp does. Since no current could result from cooling the stove, the net effect would always be positive: the stove will warm up infrequently and slightly, but heat up it will!

This new reasoning is almost correct. In fact we are on the threshold of the idea of the perpetual motion machine of the second kind. Unfortunately, the fluctuations in the temperature of the stove itself will block our efforts as they were blocked before. The stove's temperature will fluctuate up and down randomly, independently of the magnitude of the current.

But if the fluctuations in the stove are suppressed by putting it into a refrigerator, the idea will work, and heat will flow from the electric circuit into the refrigerator, but this will be a familiar heat engine with the room as the hot body.

But there is a moral to every story. Our story has one as well. Since no imp can violate the second law of thermodynamics, even if the most ingenious stratagems are used, this can only mean that the laws governing fluctuations are independent of the instruments and are determined solely by temperature, pressure, and other macroscopic parameters. It is for this reason that fluctuation measurement gives the best solution to the old problem of how to measure temperature.

The moral of the story is that no mechanical gadget can help to overcome the restrictions imposed by the all-encompassing law of entropy increase.

## Up the Temperature Scale

Let us turn back to the ideal gas. Spheres that do not collide with one another proved to be a good model for describing many of the properties of a gas in thermal equilibrium. This was the model used by physicists in the last century. It was unknown at the time that atoms are not spheres, but that they are complex systems consisting of many subparticles. It is time, therefore, to ask what the limit is up to which we can ignore the fact that atoms are composed of electrons and nuclei, and can treat them as mere material points with only three degrees of freedom. The answer is given by quantum mechanics. Electrons in an atom are not free, and their energy cannot be augmented by knocking them slightly which is in contrast to atoms which can augment their energy by colliding with other atoms or with a wall. In order to change the motion of electrons in an atom, that is, in order to change their state, the energy that must be transferred cannot be arbitrarily small but must correspond to the excitation energy of the atom. An atom, like a spin in a magnetic field, can only be in states that have strictly prescribed energies. In most atoms the excitation energy is several tenths of an electron volt and an atom simply cannot accept less. One tenth of an electron volt is approximately 1000 K. At temperatures of this order many materials begin to emit light, thus confirming the fact of the excitation of electrons.

At slightly higher temperatures (3000 K and higher) electrons can be knocked out of atomic electron shells by collisions between atoms, and become constituents of the gas together with the ions. This "exhausts" the ideal gas in the container, and the resultant mixture of electrons and ions manifests properties far removed from those of gases to which we are used at normal temperatures. The mixture of ions and electrons (of course, with a measure of neutral atoms) is called a plasma. Some time ago plasmas were a rarity as an object of study; they were encountered in gas discharge but very little was known about their properties. Nowadays a plasma is called the fourth state of matter and is the grist to the mill of those who study accelerators, astrophysics, and especially those trying to harness thermonuclear energy.

Thermonuclear plasmas are even hotter still, consisting of neutrons knocked out of light nuclei, and it is for the sake of these neutrons that the equipment used to obtain the plasmas is built. The energies of neutrons come into thousands of electron volts, that is, millions of degrees.

Of course, these are "degrees-by-convention" because these plasmas are not in thermal equilibrium and what is usually meant is the mean energy.

But nuclear fusion is not our topic, we only want to attract your attention to how the increase in plasma temperature draws new degrees of freedom into the picture. The higher the temperature, the greater the number of particles involved in thermal equilibrium. As the temperature falls, neutrons "return" to being in nuclei, and electrons again occupy their orbits. The degrees of freedom are frozen out plecisely Nernst had predicted even though he could not have guessed by any stretch of his imagination the mechanism of "freezing out of degrees of freedom". At still higher temperatures electrons and positrons are created in the vacuum as a result of collisions; this occurs at temperatures of about $10^9$-$10^{10}$ K. At temperatures of the order of $10^{13}$ K nucleons are created. Such violent processes were predominant during the early stages of the evolution of our Universe.

The temperatures mentioned above cannot be measured directly. No thermometer can be "inserted" into a plasma. Instead it is estimated from the plasma's radiation and from the energy of its particles. Millions of degrees are becoming a reality in physics laboratories.

The reader could ask, of course, where a neutron gas at one million degrees could be stored. Difficulties of this type have proved to be manageable and the gas is "suspended" in a vacuum in an intricate system of magnetic fields (called "bottles", "plugs", etc.).

In conclusion we ask another question: What is the largest temperature whose discussion (and not measurement, of course) is still meaningful? This temperature is in the list of Planck's units: $T_{\mathrm{P}} = 4 \cdot 10^{31}$ K or $4 \cdot 10^{27}$ eV $= 4 \cdot 10^{18}$ GeV.

The current opinion is that a plasma at this temperature existed at the very beginning of the evolution of the Universe. The cooling of this superrelativistic plasma, accompanied by phase transitions, created the Universe as we know it today. This is the field where science and fantasy are intertwined and is left for other books*

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*The reader is advised to read this exciting story in the book *The First Three Minutes. A Modern View of the Origin of the Universe* by Steven Weinberg, Basic Books Inc., N.Y., 1977.

## How Is Memory Lost?

Now we should make another stop, the last in this book, and ponder about the strength of the foundation on which rests the multistoried edifice of the kinetic theory of matter, or, in more modern terms, the edifice of statistical physics.

When Maxwell introduced his velocity distribution function, he well understood that none of the derivations of this function (and he devised several of them) was sufficiently rigorous. Despite all the efforts of mathematicians and physicists it was not possible to avoid a logical discontinuity in going from mechanics with its equations of motion to the Maxwell-Boltzmann theory operating with probabilities and entropy.

To solve a problem concerning the motion of a system of particles the positions and velocities of all the particles have to be fixed at some instant of time. Newton's equations then unambiguously determine the position and velocity of each particle at any other instant of time. The solution methods for Newton's equations are extremely powerful, and nowadays problems can be solved even when many particles are involved. For instance, celestial mechanics is capable of predicting the positions and velocities of the hundreds of objects comprising the solar system.

Nevertheless, among the problems encountered in the solar system Maxwell discovered some where conventional mechanics failed and statistical methods were inevitable.

Maxwell took part in a contest sponsored by the Royal Society for the best work on the nature of Saturn's rings. It was necessary to discover the properties of the rings that make them stable and prevent them from falling onto the surface of the planet or from breaking into pieces. Maxwell was able to show that a thin continuous ring revolving at a constant angular velocity would be torn apart by gravitational forces because equilibrium requires that its velocity be equal to the escape velocity at each point, and hence, that the linear velocity decreases with the radius proportional to $1/\sqrt{R}$, or equivalently that the angular velocity decreases proportional to $R^{-3/2}$. By proving in this manner that the rings cannot be continuous but must instead consist of a large number of relatively small bodies interacting gravitationally, Maxwell had to introduce probabilistic concepts into the description of the rings' behavior.

When Maxwell began the study of the behavior of gases, it was immediately clear to him that their description must be based not on mechanics, in which we monitor each individual particle, but on statistics where we are only interested in quantities averaged over a large number of particles or over a large time interval. In describing a system kinetically, coordinates and velocities are represented by distribution functions and this has proved to be a very powerful approach. An equation can be written for the distribution function, and its solution shows how this function varies in time. In the simplest case the equation is called the Boltzmann kinetic equation. Newton's equations disappeared from statistics completely.

This also cleared the theory of the coordinates and momenta of individual particles and of all the quantities usual in mechanics. When the coordinates and velocities of particles still appear such as in Brownian movement, they are essentially probabilistic quantities and are randomized by the thermal motion of the molecules.

Physical systems described by using statistical methods are called stochastic systems. If we tried to single out the most typical property in which such systems differ from ordinary systems, we should find that stochastic systems had no memory of their past.

When solving a problem in mechanics, we fix the initial conditions (e.g. coordinates of a gun and the velocity vector of the emerging projectile), and solve Newton's equations to find how they vary in time. The initial conditions thus determine the behavior of the system. By changing the initial conditions we change the fate of the system. In principle, we can solve also the "inverse" problem, i.e. reconstruct the initial data if coordinates and velocities were measured at some other time. We can say that such a system possesses memory if the initial conditions somehow survive among its other properties and can in principle be extracted at any time they become necessary. In stochastic systems the situation is quite different. The behavior of a stochastic system, such as a gas, is practically independent of its state at the initial moment of time and of the size and shape of the container enclosing the gas. Of course, some general characteristics of the system remain constant. If losses are absent, the gas's energy and momentum are conserved, but the memory of the initial energy vanishes even if friction is small. Indeed, the velocity at which a parachutist lands tells us nothing about the velocity at which he left the plane. This property of stochastic systems can be very useful in practical calculations. Thus, by postulating the loss of memory (the principle of chaos), we were able to simplify the derivation of the formulas describing the properties of a stochastic system. Thus, a gas jet filling a container quickly forgets its direction when it strikes the wall and overcomes the resistance of the gas already in the container. On the other hand, it would seem that nothing can erase the memory if the gas is regarded as a collection of elastic spheres colliding only with the walls since the motion of the spheres is completely determined by their previous collisions.

It was far from easy to answer the question about how stochasticity (i.e. chaos) evolves in a system.

For a long time it was believed that the root of stochastization was a very large (ideally, infinitely large) number of particles in the system, as well as a very complex law of interparticle interaction. The example of Saturn's rings indeed points to this explanation. Thus memory must be erased in such systems because of the very complicated character of motion. But the logic of this hypothesis is not very lucid. No simple connection is discernible between the complexity of the motion and the impossibility of extracting the initial conditions.

And it was indeed established that the conditions of many particles and long elapsed time of motion were not sufficient and were not even the principal factors required to erase the memory of the past. It proved possible to think up systems with small numbers of degrees of freedom in which memory nevertheless is lost, and this over a fairly short time.

## Lorentz's Gas

Even at the very beginning of this century Hendrik Antoon Lorentz considered a very simple model, as he was analyzing the kinetic theory of gases, which later was nearly forgotten although its properties are very instructive.

Having found that motion in three-dimensional space is unmanageably complicated, Lorentz studied the motion particles on an unbounded plane would have. The particles of his two-dimensional gas did not collide with one another, but could only collide with obstacles, namely, circles (disks) of identical radii scattered over the plane either randomly or in some regular order. He regarded each collision as elastic, so that the particles were reflected by the disks in accordance with the optical law that the angles of incidence and reflection are equal.

Calculations revealed that this simple system had some unexpected properties. Elastic impacts do not change the energy of the particles so that their velocity always remains constant and in this respect Lorentz's model differs from real gases. Though it retains the same magnitudes, the velocity of a particle changes direction after each collision so that after a large number of collisions it will move with practically equal probability (i.e. equal number of times) in each direction (for the sake of simplicity, we need speak of only two, i.e. "up-and-down" or "left-and-right" rather than every or all directions).

Of course, if everything is ideal, then the whole history of a particle's motion can be reconstructed after measuring the velocity's direction and the coordinates of the last point of impact, hence, memory does persist in the ideal case. But here a new property comes to the fore, viz. the instability of motion. If impacts are slightly inelastic, or the disks are not absolutely circular, or other perturbations creep in somewhere else, the error accumulates with each collision and the trajectories become even more stochastic.

This effect in Lorentz's gas can be described in terms that are far less vague. Assume that a narrow beam of particles is ejected from some point on the plane so that the particles are moving almost parallel to one another and the angle $\alpha$ between the velocities of any two particles is very small.

After the collisions with the fixed disks, the angle $\alpha$ will grow and quite soon all the directions will be represented equally well in the "smeared" beam. This means that the particles which were moving parallel to one another at equal velocities at the beginning, marching, so to say, in step, soon become independent, tracing very different independent trajectories and with very different velocity directions. In many cases the angle $\alpha$ between two trajectories grows exponentially with time, viz.

$$\alpha = \alpha_0 \exp \frac{t}{\tau}$$

where $\alpha_0$ is a small initial value of $\alpha$ at $t = 0$, and $\tau$ determines the rate of growth of $\alpha$ and is called the "relaxation time". We can say that the velocities in the beam "mix up", and the beam becomes stochastic after a time equal to $\tau$ by the order of magnitude.

## Mixing

The importance of mixing in statistical physics was discovered towards the end of the nineteen forties by Nikolai S. Krylov. The idea proved extremely fruitful for the explanation of the processes leading to statistical equilibrium, and in recent years the study of physical systems, which are quite diverse, as they become stochastic has turned into one of the fastest growing branches of science.

The behavior we have just discussed—the mixing of trajectories over time—is the main reason for the loss of a system's memory and thus the onset of its stochasticity after the relaxation time. In real systems, however, impacts also change a particle's speed (magnitude of velocity) and hence the system's memory for this parameter is also lost.

A major concept in the study of systems that are becoming stochastic is played by the hypothesis that their stochastic properties result from instability.

The notion of instability is usually connected with unstable equilibria. A stick balanced on its end falls down as a result of an arbitrarily small deviation from the vertical position. Suppose we stand a stick in the center of a circle drawn on the floor many times and mark the points the top of the stick strikes when it falls, then these points will lie on a different part of the circle's circumference every time we do the experiment, and after numerous repetitions the points will cover the whole circle uniformly. If the stick stood on end very accurately, the deviation from the vertical will be unnoticed to the eye. If the stick, by contrast, is balanced on the tip of your finger, fast movements by the hand or finger can stabilize the stick. The small deviations are now balanced out by the movements of the support.

Stability means that the system makes a negligible response to small perturbations of the initial conditions. A system is unstable when small changes in the initial data result in large changes in the state of the system that grow rapidly with time. Hence, the concept of instability need not only be applied to equilibria, and Lorentz's gas is an example of unstable motion. The trajectories of Lorentz's particles, which were identical in the ideal case, were mixed in a bizarre manner if the scatterers had slight "defects" and the beam relaxed and forgot the conditions at which it emerged. The circumstances required to produce chaos are not so obvious. For example, the motion of the particles can be stabilized by replacing the circular scatterers with polygons and chaos vanishes from such a system.

Other systems can be considered, in addition to Lorentz's gas, in which chaos arises with time. Yakov G. Sinai introduced another system, now referred to as Sinai's billiards.

If we surround a rectangular area on a plane by an elastic barrier, and monitor, as in Lorentz's gas, the ideal motion of the particles reflected without friction or losses from these walls, we shall see the trajectories formed of segments of straight lines. However, the directions of these trajectories will not be too entangled. If, for example, a particle was once reflected perpendicularly to the wall, it stays on this perpendicular indefinitely. However, if the boundary is not rectilinear, the situation changes drastically. By replacing the two shorter sides of the billiard table by concave circular arcs (this field is called a stadium), we change the paths of particles and stochasticize their motion. But if these sides are made convex, not concave, no chaos will be produced. The stability is related in a complex manner with the curvature of the scattering surfaces.

A large number of unstable dynamic systems were discovered when the bulky numerical calculations were made possible by large computers.

Instability in flows of gases and liquids results in turbulence.

We see that the solution to the stochasticity puzzle lies in instability, but this is not yet the final solution.

Thus, we can ask how we can determine the temperature of Lorentz's gas or of Sinai's billiards and how we can determine the number of levels and the energy in these systems. These problems are more complex and we shall not touch on them, especially since scientists themselves are not yet clear about them.

## What Is the Number of Degrees of Freedom?

The reader must have noticed that while discussing temperature in dissimilar physical situations we often modified our viewpoint on the particles of which the system was composed. First we regarded atoms as pointlike particles with three degrees of freedom corresponding to the three possible directions of motion. In other cases, atoms proved to be complex systems consisting of a nucleus and electrons, with a correspondingly enlarged number of degrees of freedom. In gas discharges, the electrons participate in the thermal equilibrium and have their own temperature which sometimes differs from that of ions (the residues of the atoms that lost the electrons). By the way, an ion which still has electrons in its outer shells is usually regarded as a pointlike particle (having, at best, only a few energy levels).

In another section we discussed the temperature of atomic nuclei the existence of whose nucleons was not even suspected by the creators of the kinetic theory. In recent years nucleons have also ceased to be regarded as elementary particles, and their constituents (quarks and gluons) are important. Many physicists are still dissatisfied with the number of elementary particles which they consider to be excessive, and they suspect that there are still more elementary particles called praquarks... The world is a very complicated system, and a simple question about the number of degrees of freedom of a particle is not so much difficult as meaningless. The old adage "a hen is but a means for one egg to produce another" becomes nearly true in the microscopic world. The classical theory of the 19th century would find itself at an impasse if it tried to determine how many degrees of freedom should one partition the thermal energy into.

However, we know that the ultraviolet catastrophe did not erupt, the day being saved by quantum mechanics which implies that all degrees of freedom enjoy equal rights in thermal motion but step into the act only at appropriate temperatures. Any degree of freedom (except translational motion) can be characterized, given one condition, by the frequency or energy of the motion. We gave you this condition for radiation when we were discussing the relationship between Planck's formula and the formulas of classical physics. It is very general: only the degrees of freedom whose energy of quantum is such that $\hbar\omega \ll kT$ can effectively participate in thermal motion. The classical condition of Maxwell that the energy per vibration in thermal equilibrium is $kT$ only holds if this energy is sufficient to produce at least one quantum. Note that this condition involves $\hbar$, whereas in classical physics the number of degrees of freedom cannot change.

The energy of the nucleons in nuclei is much higher than that corresponding to conventional temperatures. The energy of quarks is much greater still which is why they do not participate in the partitioning of thermal energy. It is also why we can ignore the profound problems of quark structure in the theory of thermal phenomena until we reach the temperatures at which stars and galaxies are born.

The lesson that quantum mechanics taught us is that not every question is meaningful, and although some questions seem to have a meaning, science needs no answers to them. This reflects the remarkable beauty and inevitability of quantum mechanics.

## Conclusion

Why is temperature still measured in degrees, whilst the amount of heat is measured in calories and not in energy units (joules)?

Physicists do not part too readily with older units of measurement, and not only because of the habit of long standing.

Although many years have elapsed since Mayer and Joule determined how many joules correspond to one calorie, it is still very difficult to measure the amount of work equivalent to a given amount of heat, especially if high accuracy is required. In principle, the ideal processes we described in this book would allow physicists to reach this objective but they are still unable to imitate a reversible process with sufficient accuracy. Therefore, the amount of heat is better measured by thermal methods, using a good calorimeter, and not by a mechanical instrument doing work.

The same is true for temperature. Even if we were able to measure the velocities of all the molecules with necessary accuracy, the calculation of temperature from the experimentally determined velocity distribution would be very complicated, and it would not be reliable. The problem becomes simple only if the gas is ideal and the velocity distribution in it is described by Maxwell's formula. But if the gas is ideal, it becomes simpler to employ the equation of state and measure temperature by a gas thermometer.

Thermal units are still very much unlike the units in mechanics. Their relation to mechanics rests in two constants: the mechanical equivalent of heat relating the calorie to the joule and Boltzmann's constant relating the degree to the joule.

A natural thermal scale will finally be established when physicists succeed in reliably measuring the work done in a thermal cycle (using the first law of thermodynamics) and organize a Carnot cycle for measuring the ratio of temperatures (using the second law of thermodynamics).

However, these two problems can be overcome by using fluctuation measurements. The probability of finding a system in some nonequilibrium state is directly related to absolute temperature. But precise measurements of fluctuations are far from easy, and the formulas relating experimentally measured quantities to temperature are considerably more complicated than the equation of state for an ideal gas.

Consequently, physicists go on living with the conventional unit, the calorie, and with agreed reference points that make it possible to calibrate thermometers identically in the same way, in all the countries of the globe.

It has already been mentioned that by convention the main reference point is the triple point of water. In addition, the calibration of master thermometers involves a number of other reference points whose temperatures are postulated to be exact. Remember, we remarked that once a reference point (and absolute zero) is established by means of a Carnot cycle, all the other points can be measured, and not assigned arbitrarily.

The values assigned to the reference points certainly agree with the most reliable measurements but by convention further improvement in measuring techniques will not affect these agreed values. Hence, the practical temperature scale will differ from the strict thermodynamic scale until the problem of measuring the amount of heat in joules is successfully resolved.

It is expedient to list in conclusion some of the reference points agreed on in 1968 and those suggested in 1976.

| | | | |
|---|---|---|---|
| Triple points: | water | 273.16 | 1968 |
| | argon | 83.798 | |
| | oxygen | 54.361 | |
| | neon | 24.559 | 1976 |
| Temperatures of transition into superconducting state: | lead | 7.1999 | 1976 |
| | indium | 3.1416 | |
| | aluminum | 1.1795 | |
| | zinc | 0.851 | |
| | cadmium | 0.519 | |

This table gives an idea of the accuracy achieved by our current temperature scale.

We are concluding our story of temperature at a point where the life of science is most apparent. As scientists move forward in their study of nature, they constantly face new and more difficult problems.

Medieval cartographers sometimes put the Latin inscription *Hic sunt leones* (*And here are wild beasts*) on their maps. It indicated regions that had not then yet been investigated. Such inscriptions seem to loom almost everywhere on physicists' maps.

In contrast to gases, science as a whole possesses memory. Everything recognized and comprehended in former periods is incorporated into the new image of the world. This book has recounted for you some of the events in the evolution of our present picture.

# TO THE READER

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# SCIENCE FOR EVERYONE

This book starts with a historical background on the notion of temperature and the development of the temperature scale. Then Ya. A. Smorodinsky covers the fundamentals of thermodynamics and statistical physics, only using concepts that will be familiar to high-school students. Having built a solid foundation, he exposes the reader to a number of phenomena that are essentially quantum-mechanical, but for which the concept of temperature “works”, and works very well. These include the spins in crystal lattices, inverse population of energy levels, microwave background radiation, black holes, and cooling antiproton beams. Although it has been written for high-school students, the book contains a minimum amount of mathematics. Nevertheless, Ya. A. Smorodinsky compensates for this severe restriction by the lucid manner in which he discusses complicated effects.

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